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ASSESSMENT OF OXYGEN DEMAND TESTS

BY



KENNETH JOHN SIMPSON

A THESIS

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled "ASSESSMENT OF OXYGEN DEMAND TESTS" submitted by KENNETH JOHN SIMPSON in partial fulfilment of the requirements for the degree of Master of Science.

Date September 28, 1970

ABSTRACT

The measurement of the oxygen demand of wastes has been a necessity in pollution control for many years. With modern treatment facilities the need is even greater for a fast, simple way of assessing effluents. Of the existing tests, namely the Biochemical Oxygen Demand, the Chemical Oxygen Demand and the Total Carbon Analyzer, none are ideal in all situations.

A relatively new test, the Oxygen Demand Index (ODI) is a chemical test which uses potassium dichromate to oxidize the organic matter in a sample of waste. A color change in the chromium from yellow to green is measured in a spectrophotometer. The concentration of color is proportionate to the organic matter in the sample and can be related to oxygen demand.

The ODI was tested for precision and applicability to pollution control and treatment facilities. It was found to be well suited for use by operators of small treatment plants. The precision of the ODI was good giving a coefficient of variation of 1.1% as compared to 4.8% for the BOD test on municipal sewage. The test also proved to be relatively insensitive to variations in test procedure.

ODI to BOD ratios varied from 1.24 to 0.61 on municipal sewage while the range of ODI to COD ratios was from 0.47 to 0.31. The variation of the ODI to BOD ratios was found to be no greater than that for the ratios of BOD to COD.

Treatment plant efficiencies were calculated using ODI values and reasonable results were obtained.

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GLOSSARY OF TERMS

Aerobic	A process or reaction involving or requiring the presence of free oxygen
Anaerobic	A process or reaction not involving or requiring the presence of free oxygen
Assimilation	The absorption and utilization of a nutrient by an organism
Biochemical Oxygen Demand	The amount of oxygen required for the biological oxidation of the organic matter in a liquid
Biodegradable	Being able to be assimilated
Biological Oxidation	A reaction whereby materials combine with oxygen through the action of microorganisms
Chemical Oxygen Demand	The amount of oxygen required for the chemical oxidation of the organic matter in a liquid (See <u>Standard Methods</u> , 1965).
Enzymes	Organic catalysts which aid metabolism
Metabolism	All essential chemical changes that occur in living organisms
Polluting Capacity	Used herein to denote the oxygen demand of a waste

CHAPTER I

INTRODUCTION

1. The Problem of Assessing the Oxygen Demand of Wastes

Ever since man first began to discharge his wastes into bodies of water, there has been the problem of how to measure the strength or the polluting capacity of those wastes. Polluting capacity or waste strength are terms which can have a variety of meanings. For example, a water may be considered "polluted" because of its color, taste, odor, temperature, radioactivity or chemical toxicity. Regardless of other indices of pollution, a prime consideration remains the water's level of dissolved oxygen. This is decreased primarily by the biological oxidation of carbonaceous organic material. A waste can then be a pollutant in this sense by virtue of its organic carbon content and its susceptibility to biological oxidation, i.e. its use of oxygen. A measure of either of these two parameters will give an indication of potential oxygen requirements or waste strength.

At one time, people were only interested in the influences of waste on the aesthetics, on the "sight and smell" of the receiving water. As man's knowledge grew, he became aware of the detrimental effects that excess pollution could have on the flora and fauna of rivers and lakes. A means to measure this pollution and hence set

control limits became a necessity. The problem is becoming more acute with the development of advanced waste treatment facilities, as now, accurate means of evaluating plant efficiencies are required.

Also, in waste treatment it is necessary to have advance warning of excess or unusual loadings coming into the plant in order that corrective action may be taken.

2. The Criteria of the Ideal Test

It follows from the above that a waste strength test, in order to be ideal, must have certain necessary conditions:

- (i) the ability to detect polluting components in a waste,
- (ii) the ability to measure those components quickly and with reasonable precision,
- (iii) the ability to enable prediction of how a stream or lake will react when the waste is introduced,
- (iv) economy and simplicity in its application.

3. Existing Tests

Of all the waste strength tests in use today, namely the Biochemical Oxygen Demand, the Chemical Oxygen Demand and the Total Carbon Analyzer, none meet all of the ideal test criteria. These existing tests will be reviewed in subsequent chapters and an attempt will be made to point out the advantages and limitations of each.

4. Oxygen Demand Index

In 1964, Arnold Westerhold of the Illinois Department of

Public Health published a paper giving the procedure for a new waste strength test called the Oxygen Demand Index. Simply, it is a chemical oxidation test using a spectrophotometer to measure a color change which is interpreted in terms of waste strength. Results are obtained in approximately 30 minutes.

It is the purpose of this thesis to analyze the O.D.I. test, to check its precision and applicability to a variety of wastes, and to compare its results to those of existing tests.

CHAPTER II

BACKGROUND AND PREVIOUS WORK

1. The Biochemical Oxygen Demand Test

The Biochemical Oxygen Demand (BOD) test is the oldest and perhaps the most thoroughly researched of all waste strength tests. It has been defined by Sawyer (1967) as the amount of oxygen required by bacteria while stabilizing decomposable organic matter under aerobic conditions. A form of the test was first proposed in the late 1800's by the British Royal Commission on Sewage Disposal, which was attempting to limit strengths of wastes being discharged into the Thames River. This test consisted of incubating diluted samples of waste water at 20°C for twenty days. By noting the difference in the dissolved oxygen in the samples before and after the test, and by taking into account the dilution, the oxygen demand of the waste could be calculated.

By 1923 the incubation period had been shortened to ten days and finally by 1933, five days was taken as the standard. Since then, the test has remained basically unchanged and is used today in most pollution control standards, treatment plant design, and effluent quality guidelines.

It is now known that BOD develops in two stages, the first or carbonaceous stage and the second or nitrogenous stage. It is only 68% of the carbonaceous stage that is measured in the standard 5 day -

20°C BOD test, the total BOD not being developed until twenty days or more. This relationship is shown in FIGURE II.1. However, it is felt by most authorities that the 5 day test is a good indication of how the waste will react in a receiving water, and that further incubation is not justified.

The carbonaceous stage can be formulated by the unimolecular equation:

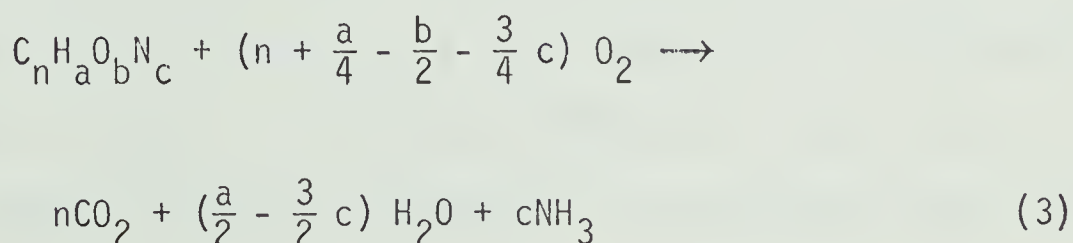
$$-\frac{dL}{dt} = kL \quad (1)$$

which when integrated gives:

$$y = L(1 - 10^{-kt}) \quad (2)$$

where y is the BOD at time t , L is the ultimate carbonaceous stage BOD and k is a rate constant dependent on temperature and the nature of the bacteria and organic matter present. The nitrogenous stage is considered too erratic to formulate mathematically.

The BOD reaction is a form of wet oxidation in which organic matter is converted to carbon dioxide, ammonia and water by micro-organisms. This reaction can be generalized in the form:



Equation (3) can be used to compute a theoretical oxygen demand (TOD) for an organic waste, although, due to the complexity of most wastes, this is seldom attempted. Instead standard solutions of simple organic compounds such as glucose or glucose-glutamic acid are used to compare TOD to results of the BOD test. BOD values are always less than TOD due to the nature of the biological oxidation reaction. The bacteria, while converting most organics to carbon dioxide, water and energy must convert some to their own cell tissue for metabolism and reproduction. These cells in turn will be converted by other bacteria after they die but in the end, the last bacterial cells will remain. Sawyer (1967) calls this humis and considers it to represent an amount of organic matter corresponding to the difference between the TOD and the BOD. This value is important when comparing the BOD to other waste strength tests.

Since the BOD depends on biological reactions of wastes which are complex in nature, it is subject to many variations both in its final measurements and in its rate of reaction. The rate constant 'k' in equation (2) will vary according to both the nature of the organic matter present and the ability of the organisms to utilize that matter. The rate of utilization will increase with the simplicity of the compound and the surface area of the particles. These changing reactions rates will in turn affect the BOD (FIGURE II.2).

While domestic sewage for a given community can be considered fairly constant in terms of constituents, industrial wastes vary considerably in nature, volume and strength. It is with the latter type

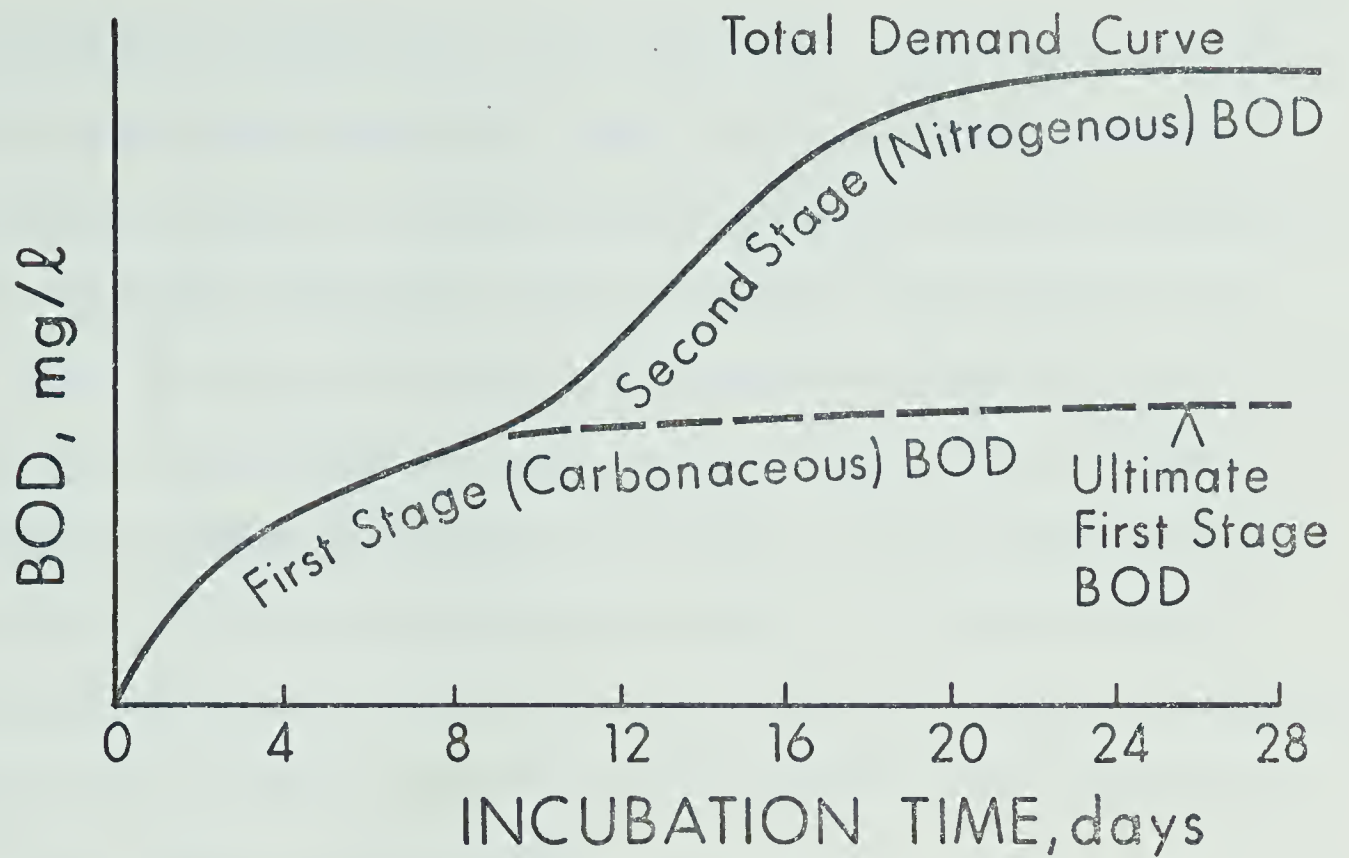


FIG. II. I GENERALIZED BIOLOGICAL OXIDATION OF ORGANIC MATTER

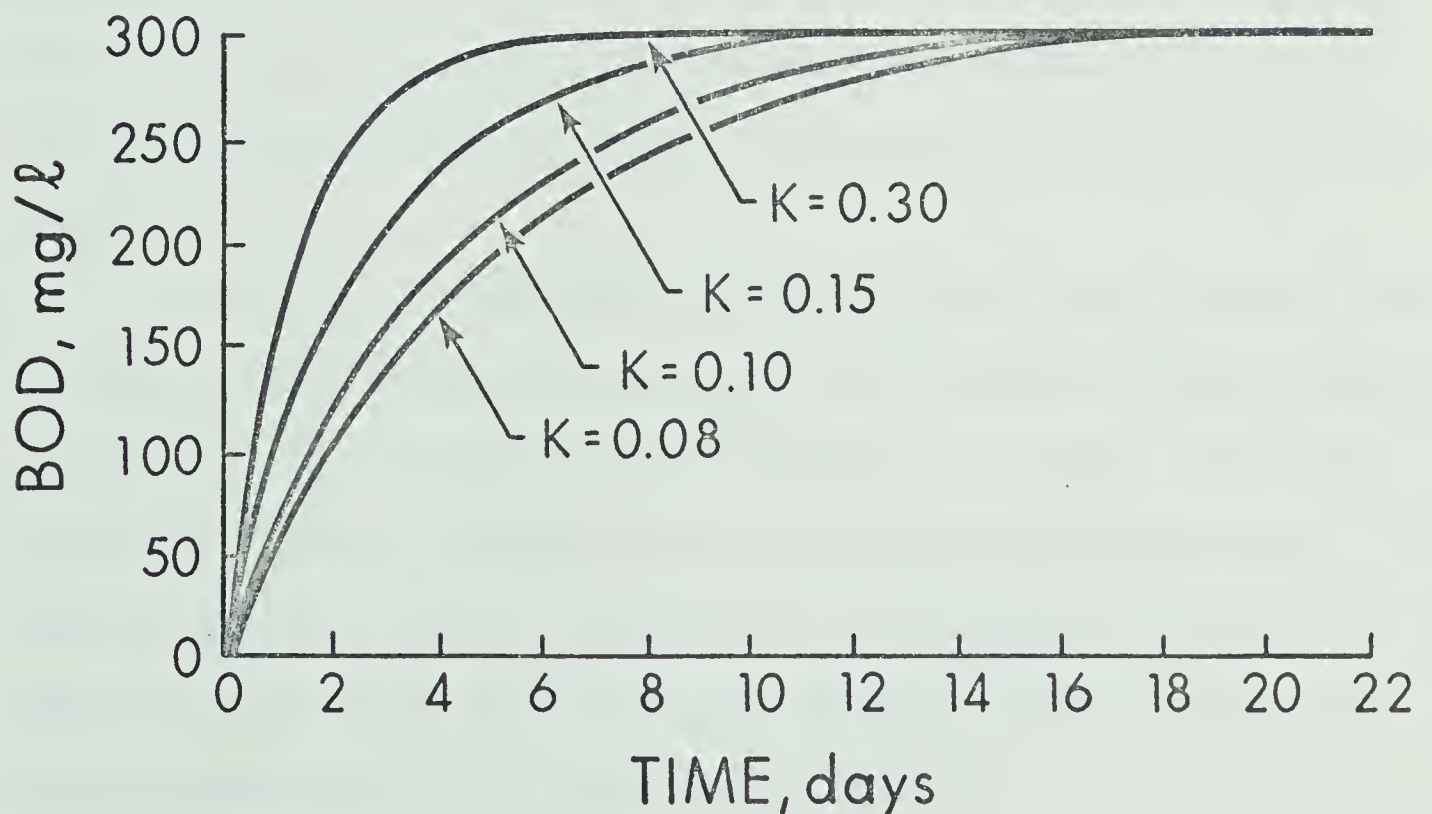


FIG. II. 2 EFFECT OF RATE CONSTANT " K " ON BOD
(AFTER SAWYER, 1967)

of wastes that the BOD test is less than ideal. Since most industrial wastes do not contain bacteria, samples must be seeded to initiate biological oxidation. This seed may not be able to utilize the material due to an enzyme deficiency and may take some days to adapt to the new food. This lag will cause low BOD readings and may be very difficult to detect. Low readings will also result if heavy metals, copper or refractory organics are present in the waste. Disinfectants such as chlorine will kill microorganisms and little or no BOD will result. Conversely, high BOD readings will result from the presence of nitrifying bacteria and oxidizable materials such as ferrous iron, sulfides and sulfites. (Standard Methods 1965)

While every effort has been made to standardize the BOD test, it remains a bio-assay, and hence semi-quantitative at best. Its most severe limitation is that of speed of results. The five day waiting period relegates the test, as far as treatment plants are concerned, to one of record keeping. It has little day to day operational significance.

Despite its limitations on precision and speed, the BOD test is the only test from which measurements of reaction rate can be made, and the only test which will detect toxicity in a waste. Since most treatment of domestic sewage utilizes biological oxidation in one form or another, and in all probability will continue to do so for many years, we cannot as yet disregard the BOD test as it is alone in providing information on biological processes.

2. The Chemical Oxygen Demand Test

Since the time of its inception, the time limitations of the BOD test have caused workers in sanitary chemistry to search for a technique that would give an indication of waste strength in a shorter period of time. It was thought that biological oxidation could be duplicated using strong chemical oxidants. Four of these in particular were investigated; namely, potassium permanganate, ceric sulfate, iodic acid and potassium dichromate. As early as 1850, potassium permanganate was used as an indicator of pollution although it was of little quantitative use. The degree of oxidation caused by permanganate varied greatly with both the compound being oxidized and the strength of the reagent itself. The fact that the "oxygen consumed" values, as they were called, were always less than 5-day BOD values showed that the permanganate was unable to carry the oxidation to any particular end point. (Sawyer 1967). Despite its lack of precision, a test using permanganate was included in Standard Methods as late as 1946.

Ceric sulfate was found by Klein (1941) to be superior to permanganate as an oxidizing agent, giving two to three times the values of oxygen consumed. Also superior to permanganate was potassium iodate investigated by Dzyadzio (1938).

However, all other methods were effectively abandoned after the classic paper by Moore et al. (1949) giving the procedure for a test in which the sample is oxidized in a boiling mixture of potassium dichromate and sulfuric acid.

This method was an immediate success since potassium dichromate

is capable of oxidizing a wide variety of compounds and also allows the excess to be readily measured by back titration. Any volatiles either originally present or formed during digestion are prevented from escaping by the use of a reflux condenser during boiling. Moore's process has been adopted as the Chemical Oxygen Demand (COD) test by Standard Methods and has changed only slightly in the past twenty years. In today's test, silver sulfate is used as a catalyst to help oxidize certain compounds particularly low molecular weight fatty acids. In addition, mercuric sulfate is added to complex any chloride ions present, since these are oxidized by dichromate and will give erroneously high readings.

A recent modification of the COD test has been proposed by Jeris (1967). Using essentially the same chemicals, the samples plus reagents are heated to $165 \pm 1^\circ\text{C}$ and immediately cooled where the excess dichromate is titrated with ferrous ammonium sulfate using ferroin as an indicator. This eliminates the two hours of refluxing as required by the standard test. Wells (1970) has evaluated the test thoroughly and finds "the small amount of special equipment necessary, the speed at which test results are obtained and the precision of the results are remarkable". He also suggests that this Rapid COD test be included in the next edition of Standard Methods. Foulds and Lunsford (1968) also found the Jeris method more precise than the standard method although absolute values were lower.

Standard Methods (1965) states that "where wastes contain only readily available, organic bacterial food and no toxic matter, the

results of the COD can be used to approximate the ultimate carbonaceous BOD values". Very few wastes however fall into this simple category, most having a wide variety of components. The COD fails to distinguish between biologically inert substances because it simply oxidizes anything that is susceptible to dichromate. A good example of this is lignin found in wood pulp wastes. It is readily oxidized by dichromate but is very inert to bacterial attack. The opposite can also be true with such compounds as acetic acid which are resistant to dichromate oxidation but are available biologically to stream organisms.

Despite the limitations, the COD test is used extensively by chemical engineers involved in treatment of industrial wastes. It is felt that the biological oxidation process is not applicable to many chemical treatment processes and as such the COD test values are used as standards in themselves. However, most municipal sewage treatment processes use BOD values as standards, as do pollution control authorities. It is therefore understandable that considerable investigation has been done to try to obtain a factor that would convert COD values into BOD values. A recent attempt was published by Wells (1970) where his BOD/COD factor was 0.477 for raw municipal sewage and 0.154 for treated municipal sewage.

He further states that "it is understandable that a different factor must be used for treated and untreated wastewater. In an untreated waste there are compounds which are subject to degradation by both biological and chemical means. Chemical oxidation with strong oxidizing agents is more complete, hence higher values are obtained

for COD than for BOD. As treatment progresses, there is a change in the ratio of biodegradable compounds to those which can be degraded by chemical means. In a well-stabilized activated sludge effluent, there are very small quantities of biodegradable compounds remaining. The ratio of chemical degradable compounds to biodegradable compounds has increased, hence a smaller numerical factor must be used to convert COD values to BOD values than is used for the untreated waste".

Many treatment plant operators, while realizing its limitations, are using the COD test to evaluate operational efficiency. They feel the rapid results, high precision and wide applicability outweigh the disadvantages mentioned previously. The test does, however, require a fair amount of chemical manipulation with complicated apparatus and many operators still hope for a simpler test that will give them the fast results of the COD.

3. The Total Organic Carbon Test

A more recently developed procedure for measuring waste strength involves an indirect measurement of the organic carbon in the waste rather than the measurement of the oxygen required to oxidize it. Larson (1964) considers this to be a more fundamental approach because carbon is a more direct characteristic of organic matter.

Various techniques have been developed to attempt to measure organic carbon, all of which are based on the total combustion of the organic matter, and the subsequent analysis of the carbon dioxide evolved. Ideas vary on the combustion technique and the method of

measuring the carbon dioxide. Methods of combustion investigated have included ultra-violet irradiation, oxygen at elevated temperatures, electric furnaces and a variety of oxidants based on chromic and sulfuric acids. The carbon dioxide has been analyzed by absorption in barium hydroxide and back titration, manometric procedures, mass spectrometry, infra-red absorption and gas chromatography (Larson 1964).

Of the numerous processes available, the most satisfactory seems to be that developed by Van Hall and his co-workers (1963, 65, 67). It involves combustion of the sample in an electric furnace in a stream of pure oxygen. The resulting carbon dioxide is measured in a non-dispersive infrared analyzer and the results are recorded as mg/l carbon on a strip chart. A flow diagram of this process is shown in FIGURE II.3.

The problem of inorganic carbon, i.e. carbonates and carbon dioxide present in the sample is solved by the use of two combustion chambers, one maintained at 950°C to oxidize total carbon, the other at 150°C to oxidize inorganic carbon only. Two runs are required, using one portion of the sample in each furnace. The total organic carbon concentration is obtained by the difference between the total carbon and the total inorganic carbon peaks on the recorder. This method is much preferred to the chemical purging of carbonates suggested by Ford (1968).

An analyzer incorporating the Van Hall process is being marketed by Beckman Instruments Inc. (Model 915). There are several of these now in use in the Province of Alberta.

Since the development of a workable TOC analyzer, considerable investigation has been done into the applicability of the results to pollution control work. Early work by Schaeffer, et al. (1965) showed the correlation of TOC values to BOD and COD to be acceptable. They state that the TOC analyzer "provides the wastewater treatment field with a practical means of quantitatively measuring the major component of organic contaminants". Good correlation was also found by Williams (1967) and Busch (1966). Busch also found that the TOC changes during biochemical oxidation could be used as a measure of biodegradable organic content. Larson (1964) published a comparison of TOC, COD and BOD for various wastes and degrees of treatment, and a study of % recoveries for various organic compounds using the three tests (TABLE II-I). Ford (1968) made an extensive study of the change in COD to TOC ratio during biological oxidation. His results are summarized in FIGURE II.4.

Very recently, two modifications of the TOC analyzer have been developed. Stenger and Van Hall (1967) have changed the carrier gas to carbon dioxide which is reduced to carbon monoxide in the combustion chamber in proportion to the organic matter present in the sample. The carbon monoxide is measured on an infrared stream analyzer and reported on a strip chart. Since carbon dioxide is a weak oxidizing agent compared to the oxygen used in the TOC analyzer, this process yields results which correlate much more closely to the traditional COD test. Stenger calls the test the CO_2D and reports its working range 10 to 300 mg/l.

TABLE II-I
COMPARISON OF TEST VALUES AS A PERCENT
OF THEORETICAL OXYGEN DEMAND

Compound	Percent of Theoretical		
	TOC	COD	BOD
Acetic Acid	102.4	97.8	74.0
Acetone	65.2	89.5	24.2
Benzene	18.6	25.1	0.0
Benzoic Acid	97.7	97.6	76.6
t-butanol	90.4	88.3	0.0
Chloroacetic Acid	90.2	100.0	0.0
Dextrose	94.3	99.3	69.2
Ethanol, absolute	107.3	94.9	65.7
Ethanol, 95%	88.6	91.4	60.8
Glycine	89.2	100.7	71.8
Lactic Acid	75.2	57.7	54.8
Methanol	97.1	96.8	55.8
Monosodium Glutamate	108.4	106.8	60.5
Oxalic acid	96.8	99.9	45.9
Phenol	94.0	99.4	61.0
Pyridine	56.6	3.7	0.0
ABS 84%	78.0	79.6	0.0
Succinic Acid	101.2	100.0	62.9
Sucrose	96.1	97.6	61.4

After Larson (1964)

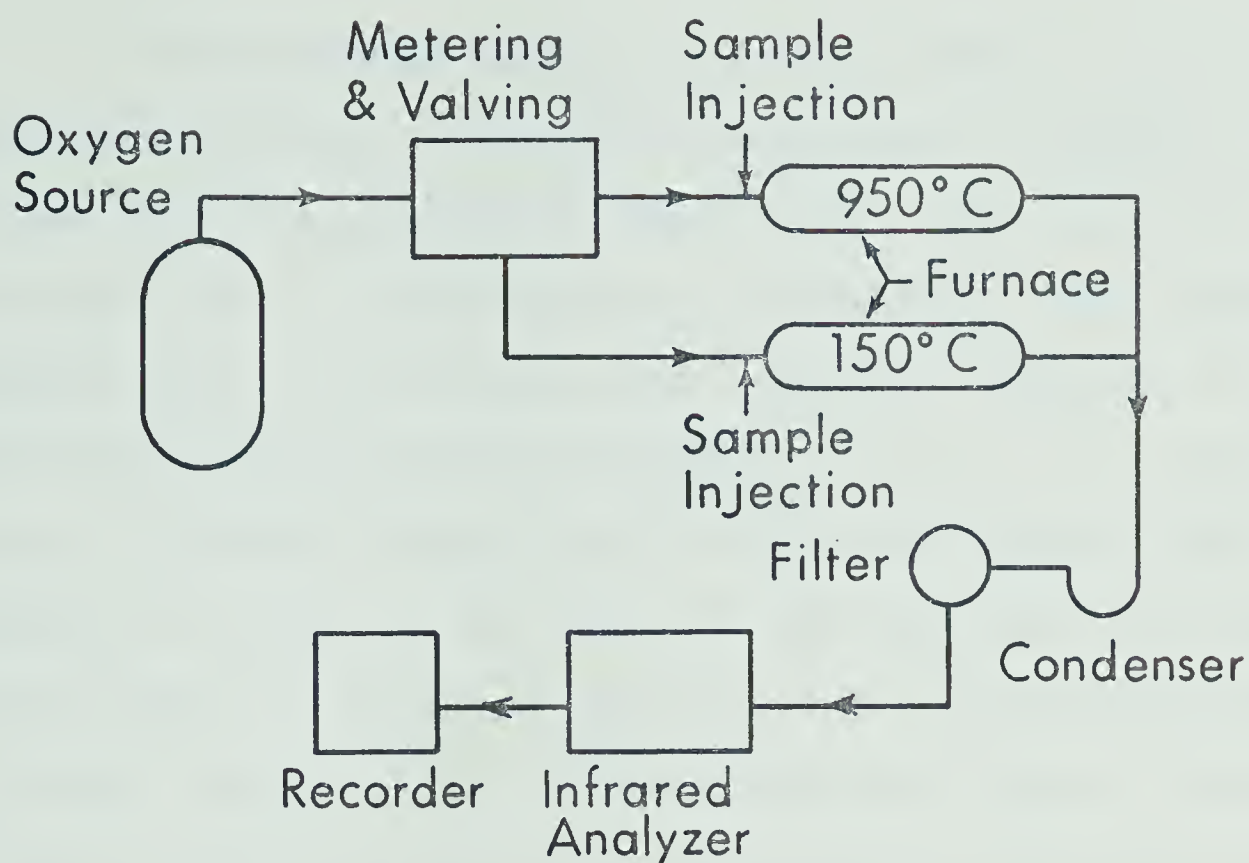


FIG: 11.3 FLOW DIAGRAM OF TOTAL CARBON ANALYZER

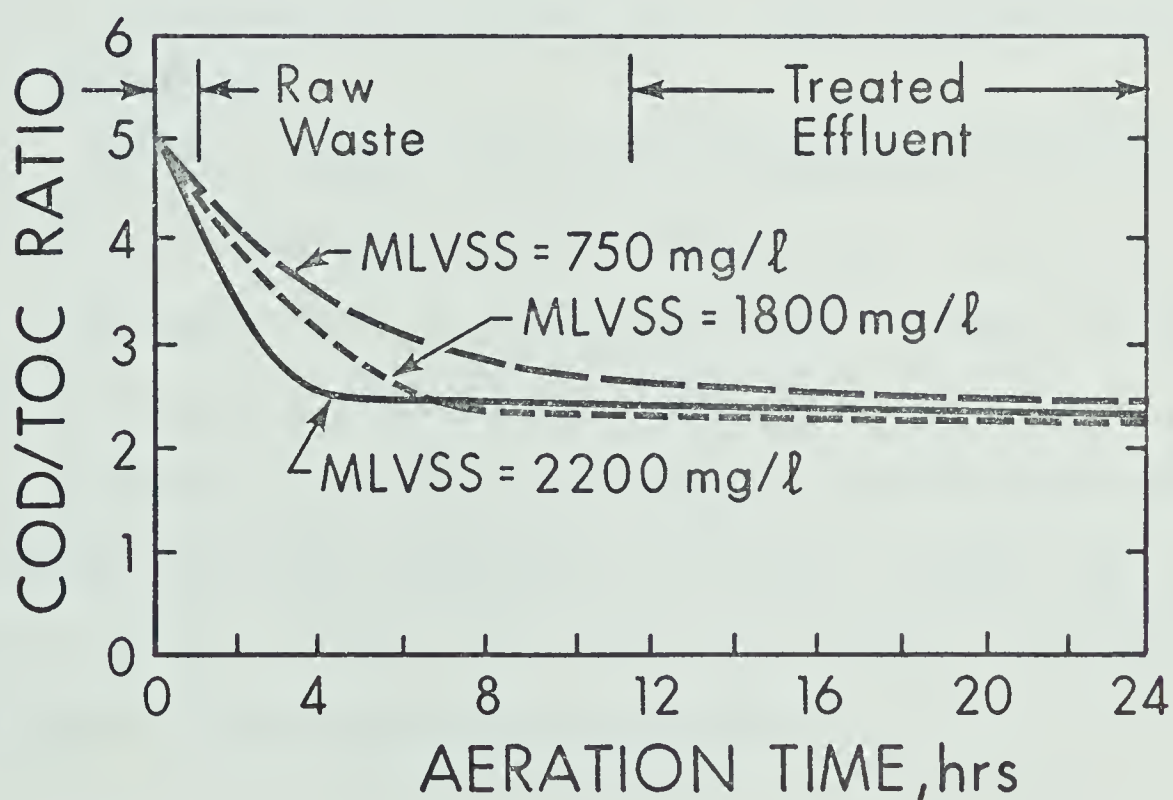


FIG: 11.4 VARIATION OF COD/TOC RATIO WITH DEGREE OF BIOLOGICAL OXIDATION (after Ford 1968)

A new instrument developed by Clifford (1968) is the Total Oxygen Demand analyzer. Here again the carrier gas is changed, now being nitrogen containing approximately 200 ppm oxygen. Hill (1969) describes the process thus ; "As the carrier gas and sample pass over a heated platinum catalyst, two reactions occur: first, the impurities in the sample are oxidized by partially depleting the oxygen on the platinum surface, and second, the oxygen equilibrium on the catalyst surface is restored by the oxygen in the flowing carrier gas stream. The second reaction results in a momentary depletion of the oxygen in the carrier gas stream. Carrier gas and oxidized samples pass through a scrubber to remove interfering compounds and then through a silver-lead fuel cell detector. The trace oxygen detector system measures the depletion of oxygen as a result of regeneration of the catalyst and this is recorded as a peak, actually a negative peak since the oxygen concentration is decreasing".

The TOC analyzer, and its later modifications, certainly appear to be an improvement over the classic tests. The only limitation seems to be that of cost. A price range of \$10 - \$12,000 plus the necessity of having a fully trained technician to operation it, puts the carbon analyzer only within the reach of large treatment plants and research and control authorities. The small treatment plant operator will not be able to make use of this advanced technology, even though it would surely be of use to him.

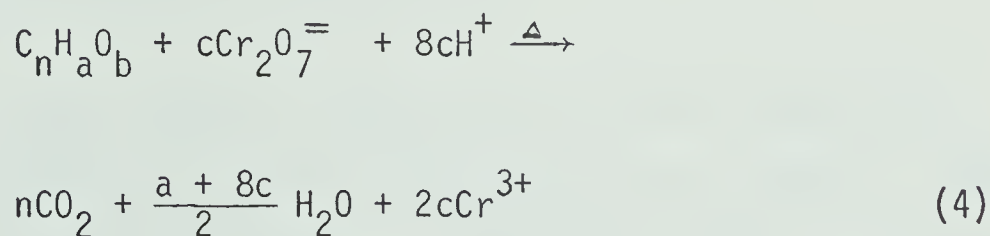
CHAPTER III

THE INVESTIGATION

1. Theory of the Oxygen Demand Index Test

The Oxygen Demand Index test (ODI) is basically a chemical oxidation of a sample of waste using reagents similar to those used in the COD test. However, instead of refluxing and back-titrating as with the COD, the samples are placed in boiling water for 20 minutes, after which values of percent transmittance of light through the sample are obtained using a spectrophotometer. The amount of oxygen required for chemical oxidation is then obtained by comparison with a calibration curve.

The oxidizing agent is potassium dichromate in a solution of sulfuric acid. The reaction of dichromate with a generalized organic compound is given by Sawyer (1967) as:



where

$$c = \frac{2}{3} n + \frac{a}{6} - \frac{b}{3}$$

In this reaction, the organic matter in the samples reduces the hexavalent chromium which is of a characteristic yellow color, to

the trivalent state which is green. The degree of this color change will give a proportionate indication of the amount of carbonaceous organic matter in the sample.

This degree of color change can be measured colorimetrically since the reaction mixture follows the Beer-Lambert law:

$$T = \frac{I}{I_0} = 10^{-kcl} \quad (5)$$

or

$$A = \log \frac{I_0}{I} = kcl \quad (6)$$

where

- I_0 = intensity of light entering the solution
- I = intensity of light leaving the solution
- T = transmittance of solution
- A = absorbance or optical density of solution
- k = constant for a particular solution
- l = length of absorbing layer
- c = concentration of the solution

The law states that the intensity of a ray of monochromatic light decreases exponentially as the concentration and length of light path of the absorbing medium increases. Westerhold (1964) suggests using a spectrophotometer set at a wave length of 600 mu when testing the samples, as this gives the highest sensitivity in the yellow-green range. A purely hexavalent (yellow) solution, produced by using dis-

tilled water in place of an organic sample, is used to set 100% transmittance on the spectrophotometer. Any organic matter in subsequent samples will turn the samples green, and absorb a proportion of the 600 mμ light according to the Beer-Lambert Law. Hence, all samples containing more organic matter than the distilled water blank will give readings of less than 100% transmittance.

Quantitative results are obtained by running a series of known concentrations of a simple organic compound and plotting percent transmittance vs. concentration on semi-log paper. If the reaction mix follows the Beer-Lambert Law, the plot will be a straight line. The 5-day BOD of the compound is then found and related to its concentration. This BOD per volume is then used on the arithmetic scale of the semi-log plot in place of the concentration values. A commonly used standard solution is 600 mg/l of glucose which gives a 5-day BOD of 450 mg/l. Since the ODI test uses a 5 ml sample, the color intensity of 5 ml of this standard glucose is used to represent a BOD value of 450 mg/l. A 5 ml sample of waste having the same color intensity is taken as having an ODI value of 450 mg/l. It follows that if 1 ml of the standard glucose is used (brought up to 5 ml with distilled water to keep volumes constant) the ODI value will be 90, i.e. 90 mg/l per ml. A calibration curve, made by running 1.0, 2.0, 3.0, 4.0 and 5.0 ml of standard glucose is shown in FIGURE III.1. Samples of any organic waste can then be tested and by referring to this calibration curve a corresponding "glucose BOD" or Oxygen Demand Index (ODI) can be found. Westerhold (1964) states that "on samples containing biodegradable

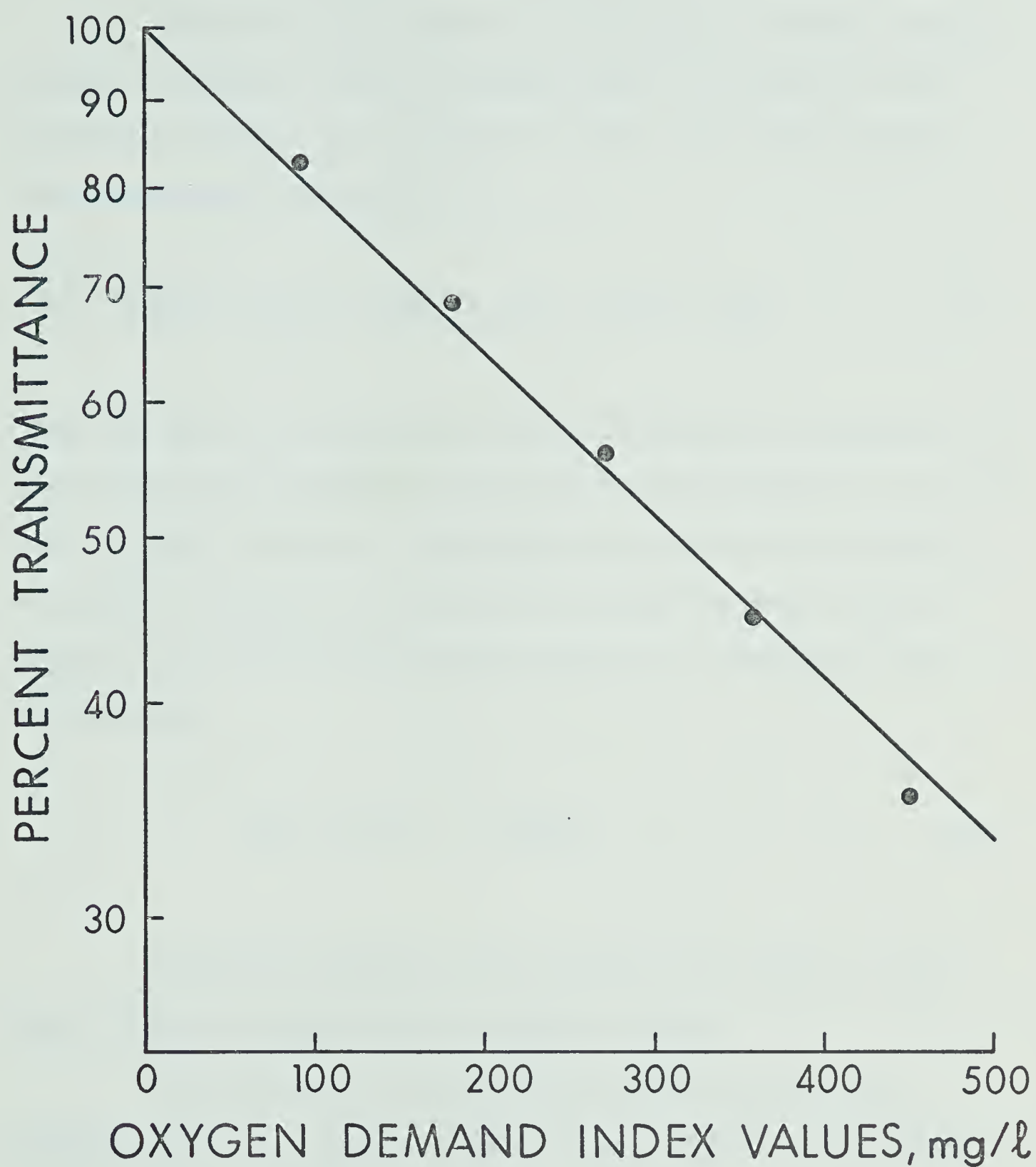
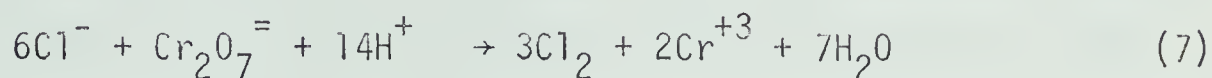


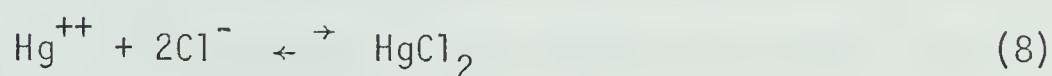
FIG: III.1 CALIBRATION CURVE FOR THE ODI TEST
(after Westerhold 1964)

material, the ODI values should be roughly equivalent to BOD values".

Two serious limitations of the dichromate oxidation process are that it oxidizes inorganic chloride ions, and secondly, it will not oxidize straight chain alcohols and acids. The former problem can be represented by equation (7)



Since this gives the same green trivalent chromium ions as Equation (4) it will give the indication of more organic matter present in the sample than is actually the case. Fortunately the problem can be solved by the addition of mercuric sulfate which according to Sawyer (1967), complexes the chloride ion and thus prevents its interference with the dichromate.



The mercuric sulfate must be added to the sample of waste before the other reagents and is usually in excess.

The oxidation of straight chain alcohols and acids by dichromate requires a catalyst, namely silver sulfate, usually added to the sulfuric acid which is used in the test.

2. Experimental Procedures

In any experimental work in which values are to be compared, it is especially important that standard procedures be followed in all cases. With older established tests such as the BOD and COD, this presents no problem since Standard Methods gives specific details and instructions which cover all situations. The eleventh edition (1965) was used in this work for all procedures involving the BOD and COD.

For the Total Organic Carbon test which was run on a Beckman Model 915, manufacturer's instructions had to be relied upon, since no accepted standards are yet available. During the experimental period, several problems arose. Since the injector syringe needle was only capable of passing particles of 170 microns diameter or smaller, all samples had to be blended before use. It was found that 5 minutes at 45,000 rpm on a Vir Tis Model 45 homogenizer was sufficient to reduce any waste to a fine dispersion which easily passed the needle. For comparison, BOD's, COD's and ODI's were also run on these blended samples.

It was found that injection technique was very critical and it was important to have the same technician run all samples in a batch on both the total carbon and total inorganic carbon furnaces. Standards were run every 5 to 10 samples to check both the machine and the operator's technique. This procedure gave results that were reproducible within $\pm 2\%$. It was found that linear, and hence most precise, results were obtained in the range 0 - 100 mg/l and suitable dilutions were made using de-mineralized water to keep the readings in this range.

The procedure for the Oxygen Demand Index has not been standardized although Westerhold (1964) gives a fairly detailed account in his original paper. This detailed procedure can be found in Appendix A.

For this investigation of ODI, reactions were carried out in 1 inch diameter optically similar Nessler tubes in which the percent transmittance was found to vary no more than $\pm 1\%$ among tubes. Five ml samples were measured into each tube using a five ml Mohr pipet. Since all raw sewage was blended before use, a wide tip pipet was not required. Five ml of distilled water was placed in one tube to act as a blank. Approximately 0.1 grams of mercuric sulfate was added to each sample using a scoop. Any excess amount of mercuric sulfate did not affect the ODI readings, but depending on the sample took longer to settle and delayed the reading. Using a 5 ml Mohr pipet, 1.50 ml of 0.25 N potassium dichromate was added to each tube. This amount was found to be very critical and good pipetting technique was required. Finally 7.5 ml of concentrated sulfuric acid containing silver sulfate was measured into each tube. An automatic acid buret was used for this purpose and found very satisfactory. Ordinary pipets could be used but due to the high viscosity of the acid, the process is very tedious with the constant risk of spillage. Although not as critical as the dichromate measurement, the amount of acid will affect the dilution and hence the concentration of color in the sample. The tubes were then placed in a test tube rack in a pan of boiling water for 20 minutes. A bunsen burner was used as a heat source since an

ordinary laboratory hot plate would not keep the water at a rolling boil. The level of the water was kept at least over the level of liquid in the tubes to ensure total heating. For the high temperature experiments a Fisher high temperature bath filled with vegetable oil was used. Other fluids such as paraffin, ethylene glycol, and glycerin were tried and rejected. The only objection to the oil was that it could not be easily cleaned from the tubes and the reaction mix had to be transferred to clean Nessler tubes before reading in the spectrophotometer. A special rack was constructed to fit in the high temperature bath, hold the tubes, and allow free heat transfer from the bath to the oil. A thermometer was suspended in the oil in one of the tubes spaces to record the emersion temperature as the thermostat reading on the high temperature bath was found to vary $\pm 8^{\circ}\text{C}$.

After 20 minutes heating time the tubes were transferred to a container of ice water where they were allowed to cool for 10 minutes. Using a Baush and Lomb "Spectronic 20" set at a wave length of 600 μ , the percent transmittance of each sample was read, using the blank for 100%. Some samples which contained particulate matter or turbidity had to be left longer than 10 minutes in order that they could clear. All samples cleared in time, none taking longer than 45 minutes. It was quite obvious when a sample was not clear and any attempt to take a reading resulted in gross error. Using the values for percent transmittance, ODI values were read off the standard glucose calibration curve originally prepared by Westerhold (1964).

3. Observations and Results

The experimental work concerning the ODI test was conducted in two phases. Phase one dealt with the test itself; its precision, reproducibility, and the effect on test values of varying certain elements such as boiling period, time before reading and emersion temperature. Phase two involved comparing the results of the ODI test with those of the BOD, COD and TOC tests for as many varied wastes as possible in order to assess its applicability to pollution control work.

(a) Phase One Data

TABLE III-I shows the variation in percent transmittance among portions of the same sample run under identical test conditions. It was intended that these tests would indicate the precision of the ODI test since ODI values are read directly off the calibration curve using percent transmittance values. With the standard glucose solution, the standard deviation of the nine samples was 0.48 while with the more complex sewage sample the standard deviation of seven samples was 0.85. The percent standard deviations or coefficients of variation for the glucose and sewage were 0.99% and 1.1% respectively. For reproducibility with 99% confidence, the glucose mean $\pm 2.6\%$ can be taken while for the sewage the mean $\pm 2.9\%$ is sufficient. For comparison, BOD tests by Wells (1970) gave coefficients of variation averaging 3.2% for glucose and 4.8% for sewage. The reason the values for sewage have a larger scatter than those for glucose is most likely the relative non-homogeneity of the sewage compared to the glucose. Even

TABLE III-I

PRECISION OF THE OXYGEN DEMAND INDEX

Replicate samples run under identical conditions

Sample Number	Standard Glucose (% Trans.)	Primary Sewage (% Trans.)
1	49.0	76.5
2	49.0	76.0
3	48.5	77.0
4	49.5	76.0
5	49.0	75.5
6	50.0	75.0
7	48.5	77.5
8	49.0	--
9	49.5	--
Mean	49.1	76.2
Standard Deviation	0.48	0.85
Coefficient of variation	0.99%	1.1%

though care was taken to ensure that all samples were uniform some would inevitably contain more or less of certain compounds which would be attacked to a greater or lesser degree by the dichromate oxidizer. The glucose samples which were homogeneous would not be subject to these fluctuations in oxidation rates and the deviation of the test values about the mean would be due only to test and technique errors. The figure for 99% confidence limits is therefore more meaningful for the glucose than for the sewage.

The Oxygen Demand Index test was first proposed by its developer as an aid to operators of small treatment plants and lagoons. Used under these circumstances, it is likely that the test would be run by semi-skilled or un-skilled personnel who might not appreciate the need for standard procedures. With this in mind a series of tests were run in order to evaluate the effects of deviating from the given procedures and to ascertain which of these procedures, if any, were critical.

In order to study the effect of varying emersion temperature, samples of standard glucose and primary sewage along with a blank for each set were heated for 20 minutes at temperatures from 22°C to 165°C. FIGURE III.2 shows the variation in percent transmittance with temperature when all samples are run against the 100% transmittance of the blank heated in boiling water. No significant change in transmittance was noted for emersion temperatures of 22°C to approximately 95°C. With still higher temperatures, a marked decrease in percent transmittance was observed in all three samples, caused by a darkening of

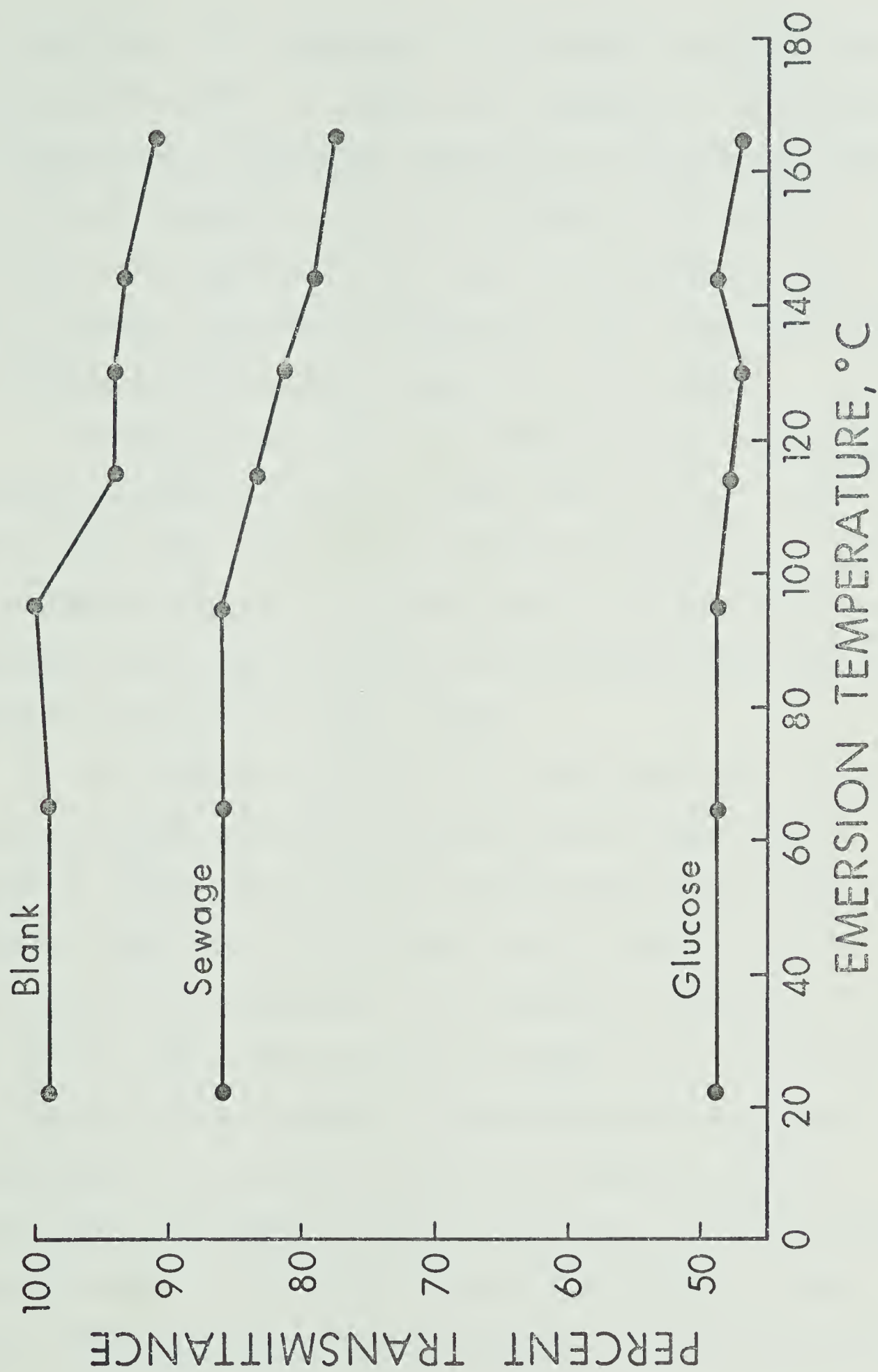


FIG: III.2 VARIATION OF % TRANSMITTANCE WITH EMERSION TEMPERATURE
(100% set from 95° C blank)

the reagent mix. This darkening of the dichromate solution is discussed by Wells (1970). If however, the darkening of dichromate is accounted for by setting the transmittance of the blank at 100% for each test temperature, the plot of FIGURE III.3 is obtained. In this case it is seen that the test values form a much more linear path. In effect, the emersion temperature is not critical as long as the blank is heated to the same temperature as the sample.

Another factor which it was thought might be inadvertently varied was the period of time the samples were to be left in the boiling water bath. The procedure specifies 20 minutes but it was found (FIGURE III.4) that varying the period in the bath from 0 to 85 minutes had no significant effect on the percent transmittance of either the glucose or the sewage samples.

As mentioned in section III-2, particulate matter, especially mercuric sulfate and chloride precipitates took a finite time to settle out and no accurate reading could be taken until this had occurred. A series of tests were run to estimate the time required for this settling and also to determine if the time before reading was critical. The results of these tests are shown in FIGURE III.5. It can be seen that immediately after removal from the boiling water the percent transmittance was relatively low due to the dispersion of the insoluble salts which deflect a portion of the light. As time progresses, these salts settle out and the readings of transmittance of light reach a maximum and remain there indefinitely. In effect the waiting

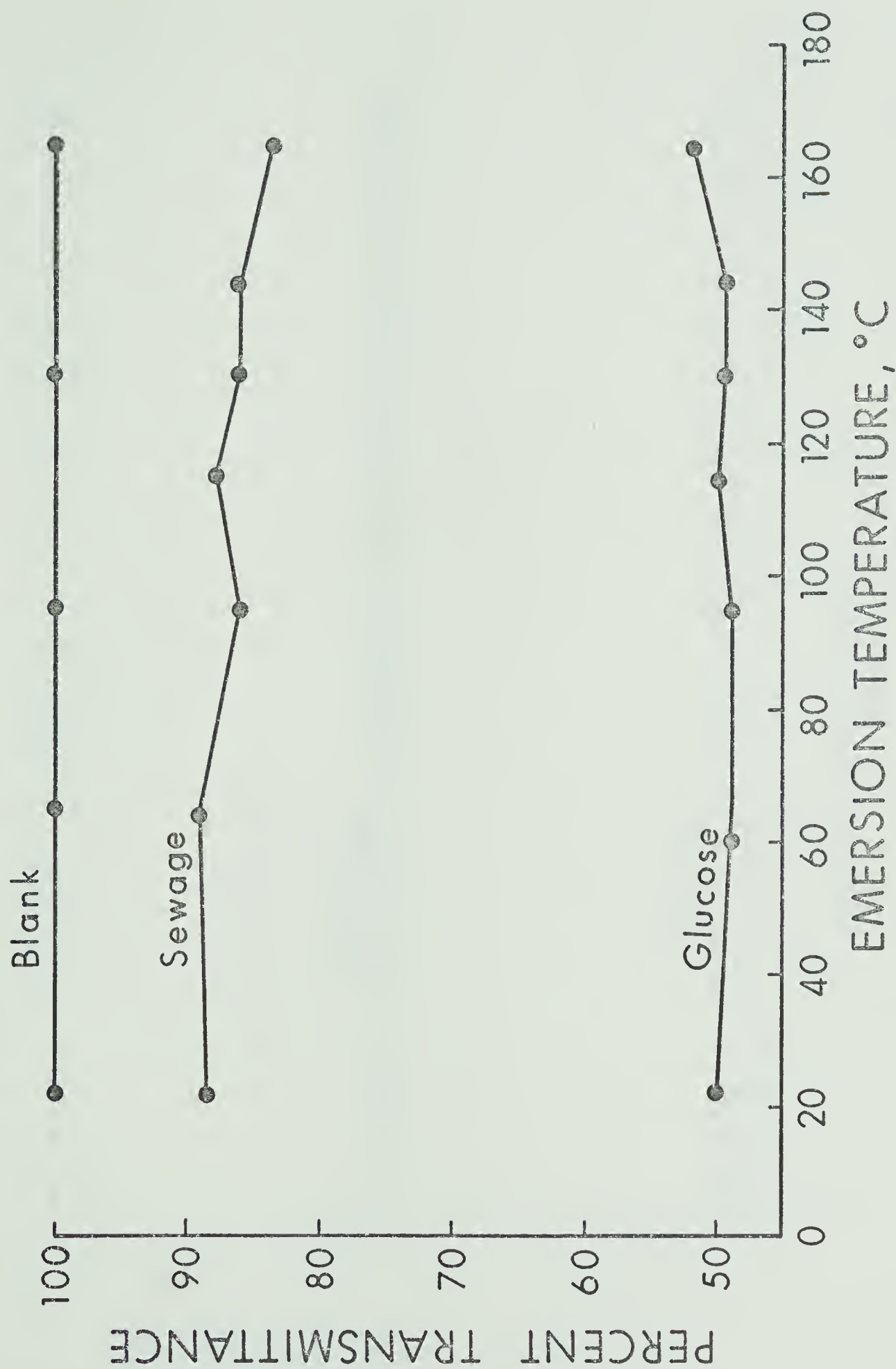


FIG: III.3 VARIATION OF % TRANSMITTANCE WITH EMERSION TEMPERATURE
(100% Set from blank at each temperature)

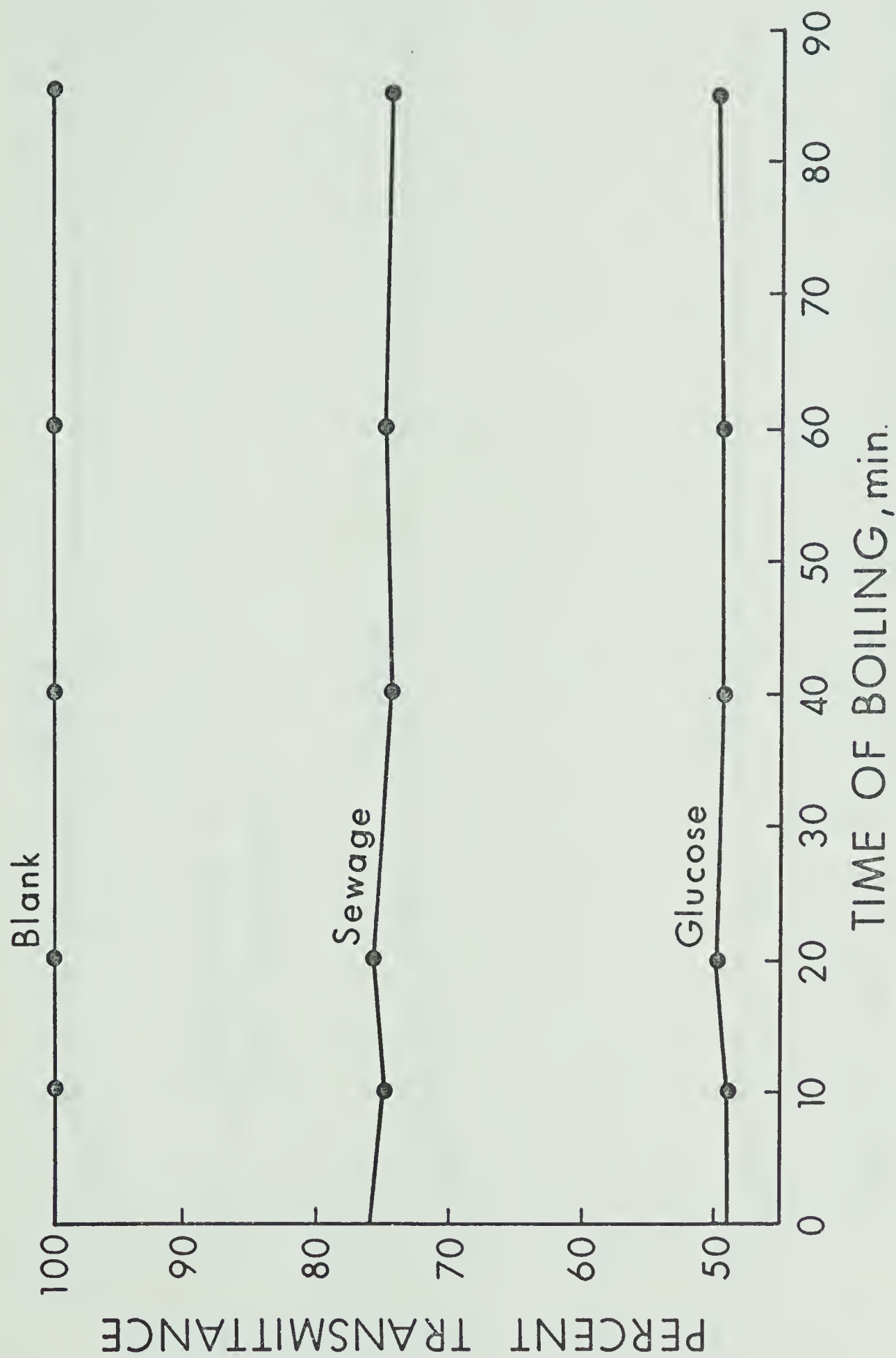


FIG: III.4 VARIATION OF % TRANSMITTANCE WITH BOILING PERIOD
(100% set from blank at each time period)

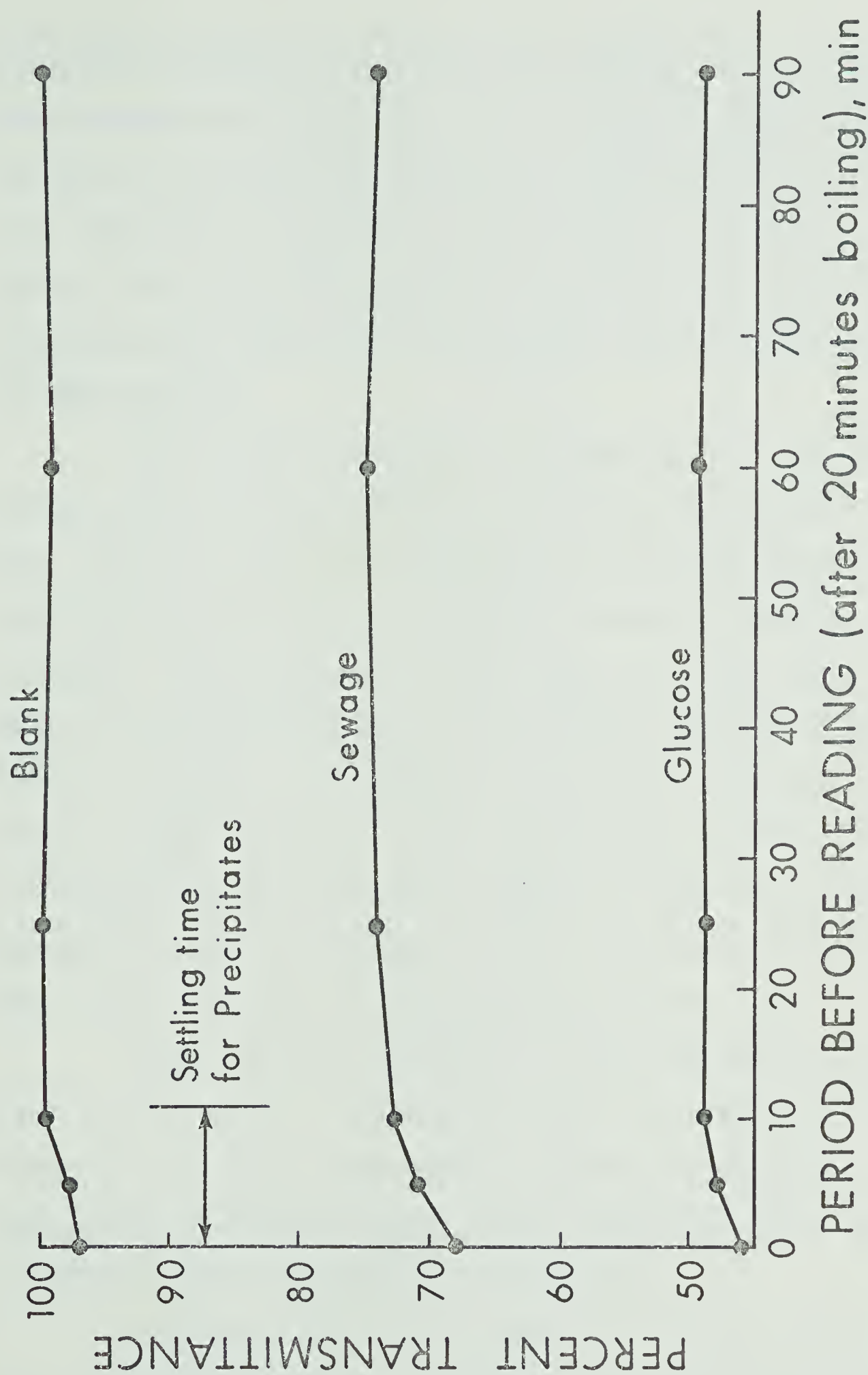


FIG: III.5 VARIATION OF % TRANSMITTANCE WITH LENGTH OF PERIOD BEFORE
READING (100% set from 10 min. blank)

period before reading has no effect on the reading as long as complete settlement has taken place. This time of settlement is about 10 minutes for the quantities of chemicals specified in the test. It was found that if more than 0.1 gram of mercuric sulfate were used or if the samples were agitated during or after the period in the boiling water, longer than 10 minutes was required for settlement.

(b) Phase Two Data

It is possible for the ODI or any new test to be applicable to general pollution detection and control work in two different ways. The first is that it be acceptable as an absolute standard in itself whereby workers become accustomed to thinking in terms of ODI values. The second way is that ODI values are thought of in terms of older established tests and the mental conversion to BOD or COD is always made. The absolute standard phase rarely comes about without a lengthy acceptance or familiarization phase preceding it. The following experimental work was attempted in order that the ODI test may become more familiar through comparison with established tests, whether it becomes an absolute standard or not.

The ODI test was compared with the BOD, COD and TOC on many wastes in the province. Included were Edmonton raw and primary sewage, Calgary raw and primary sewage, Devon raw, primary and secondary sewage, Leduc anaerobic and aerobic sewage lagoons and a cross section of industrial wastes from Edmonton and Calgary.

In general, the ODI did not compare in absolute values with any of the established tests. FIGURE III.6 shows the comparison of

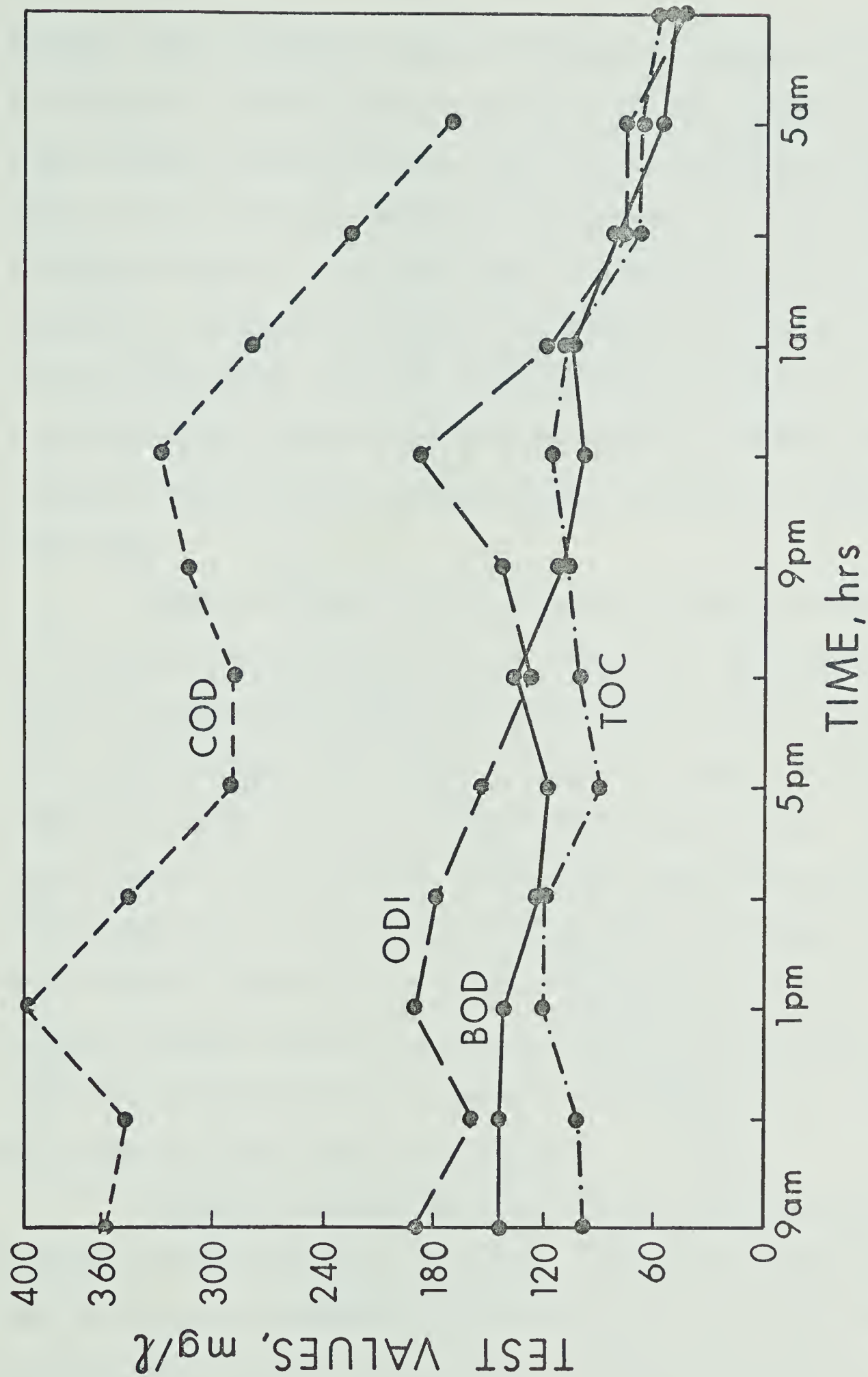


FIG: III.6 COMPARISON OF OXYGEN DEMAND TEST RESULTS - 24 HR. RUN FROM CALGARY RAW SEWAGE - JUNE 1970

ODI, BOD, COD, and TOC test values on Calgary raw sewage during a 24 hour period. While trends are generally followed it can be seen that no single conversion factor exists. The ODI seems to follow the COD as far as sensitivity to change is concerned but it approximates the BOD more closely in absolute values. An interesting aspect of this plot is the way the strength of the sewage varies with the time of day. Allowing for flow time in the collection system, major activities of the population can be noted such early morning rising and evening dinner with the weakest sewage as expected in the hours before dawn.

Appendix B contains detailed tables and plots of comparative data on the ODI and established tests. FIGURE III.7 is a summary plot of a portion of this data showing the range of values of the ratio of ODI to BOD. This is seen to vary from a high of 1.24 for Calgary raw sewage to a low of 0.61 for Devon final effluent. The closest value to unity was that for the Leduc sewage lagoons where both the anerobic and aerobic effluents gave BOD values equal to ODI. This plot emphasizes the fact that the complex nature of municipal sewages prevents them being classed as a single waste. Each particular waste source must be analyzed individually, and no single ODI to BOD ratio will apply to all wastes.

FIGURE III.8 summarizes the various ODI to COD ratios for municipal sewages obtained in the study. As would be expected since both tests use a dichromate oxidizer, the range of the ratios is not as great as with the ODI to BOD ratios. It varies from 0.47 for

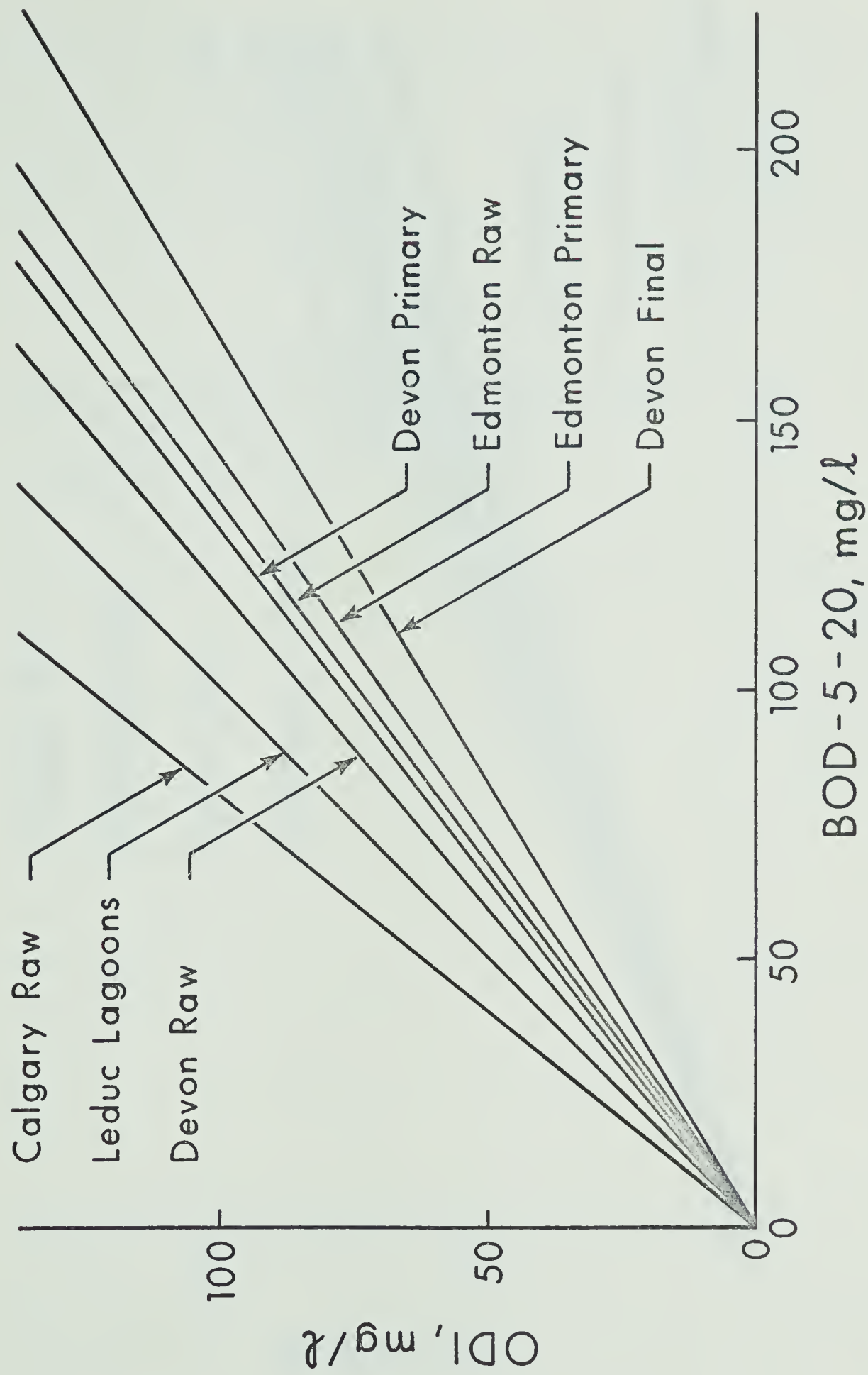


FIG: III.7 SUMMARY PLOT SHOWING VARIATION IN ODI TO BOD RATIOS FOR VARIOUS MUNICIPAL SEWAGES (from Appendix B)

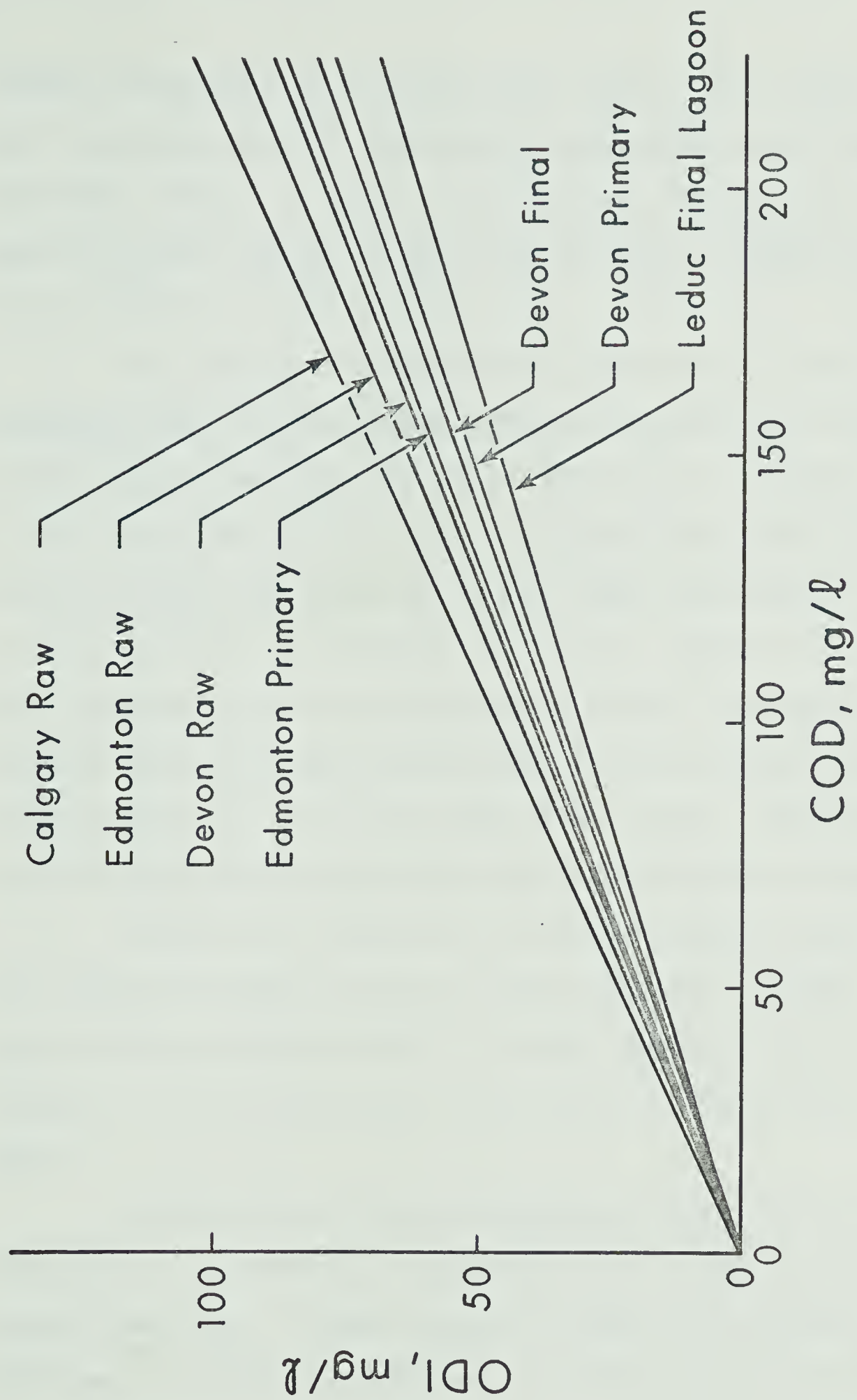


FIG: III.8 SUMMARY PLOT SHOWING VARIATION IN ODI TO COD RATIOS FOR VARIOUS MUNICIPAL SEWAGES (from Appendix B)

Calgary raw sewage to 0.31 for the Leduc lagoons. This range is still too large to try to fit a single ratio to all wastes and, as before, individual analysis is required. The detailed data and plots from which the above summaries are taken can be found in FIGURES B.1, B.2, B.3 and TABLES B-I, B-II and B-III.

The purpose of finding ratios of test values is that an unfamiliar test value can be put in terms of a more familiar one. This is done quite extensively with COD and BOD ratios in treatment plants. It was thought that it would be of use to know which ratio varied the least, the BOD to COD or the ODI to BOD. TABLE B-IV shows the coefficients of variation for different tests ratios computed from the means and standard deviations given in previous tables. As expected the ratio of ODI to COD gives the least variation at 14.4% while the ratio of BOD to COD was 21.8% and ODI to BOD, 18.4%. Individual wastes however varied considerably and no trend could be visualized.

TABLE B-III includes data on the total organic carbon analyzer for Calgary raw sewage as well as various industrial effluents. The plot of TOC versus BOD and ODI for municipal sewage is shown in FIGURE B.4. The following table (III-III) is a summary of the above data.

Another area of the investigation was one which tried to determine which components of sewage were most influential on the oxygen demand tests. Sewage consists of organic and inorganic solids which may be suspended or dissolved. For this work dissolved solids were defined as those passing through a glass fiber mat in a Gooch

TABLE III-II
SUMMARY OF TEST RATIOS ON CALGARY RAW SEWAGE

RATIO	$\frac{\text{BOD}}{\text{COD}}$	$\frac{\text{ODI}}{\text{BOD}}$	$\frac{\text{ODI}}{\text{COD}}$	$\frac{\text{BOD}}{\text{TOC}}$	$\frac{\text{COD}}{\text{TOC}}$	$\frac{\text{ODI}}{\text{TOC}}$
Mean	0.38	1.24	0.47	1.15	2.97	1.42
Coefficient of Variation	13%	15%	9.4%	21%	14%	21%

For comparison, industrial waste ratios of ODI to TOC ranged from a high of 2.10 for a chemical plant to a low of 0.58 for a brewery effluent. The same brewery on a different day gave the ratio as 1.44 which points out the complexity and unpredictability of industrial wastes.

crucible under vacuum. The suspended solids were those retained on the mat, usually the particulate matter. By separating the organic fraction of the solids into suspended and dissolved, the oxygen demand tests could be run on each separately. In effect the suspended organic solids were obtained by the difference between the total organic and the dissolved organic. TABLE B-V and FIGURE B.5 show the results of these tests. The differences between biological oxidation and chemical oxidation become apparent. It appears the BOD values depend more on dissolved than on suspended solids while the opposite holds true for both the ODI and COD tests. This may be due in part to the fact that dissolved solids are more readily available for assimilation by microorganisms than are particles. In chemical oxidation the boiling acids oxidize all organic solids re-

ardless of particle size.

The town of Devon which has one of the few trickling filter sewage treatment plants in Western Canada, was chosen for the phase of the experimental work dealing with treatment plant efficiencies. The question of how well a plant is removing the oxygen demanding material from a waste is usually answered with a simple formula using BOD's. The percent removal is the incoming BOD minus the outgoing BOD divided by the incoming BOD (expressed as a percentage).

$$\% \text{ Removal} = \frac{\text{BOD}(\text{in}) - \text{BOD}(\text{out})}{\text{BOD}(\text{in})} (100) \quad (9)$$

This method of calculation of efficiency is used almost universally despite the fact that by the time the efficiency is known, the effluent is five days downstream. If the ODI test, which gives results in 30 minutes, could be used in calculating efficiencies, it would enable better plant control. To this end, four separate runs were made on the Devon plant using both the primary and the secondary effluents. The results of these tests are shown in TABLE B-VI. It was found that ODI efficiencies were higher than the BOD efficiencies by about 12% on the primary and 7% on the secondary effluents.

TABLE B-VII is a list of miscellaneous data provided by the Environmental Health Services Laboratory. It is included here since it shows again the variety of industrial wastes and the difficulty of setting a single conversion ratio to any group.

CHAPTER IV

SUMMARY AND CONCLUSIONS

The purpose of this thesis has been to review the established tests for measuring the oxygen demand of wastes and to analyze the relatively untried Oxygen Demand Index test in the context of the older tests. It was particularly intended to investigate the applicability of the ODI test to use in smaller installations where BOD tests have been proven too slow, COD tests too complicated, and TOC tests too expensive.

In phase one of the experimental work, the ODI test appeared well suited for the semi-skilled operator. Its precision compared favourably with that of the BOD test, giving a coefficient of variation 1.1% as compared to 4.8% for BOD on municipal sewage. (TABLE III-I) The effects of a chance variation in test procedure were in general not serious. The temperature at which the samples were heated (for 20 minutes) was shown not to be critical as long as the blank was heated at the same temperature (FIGURE III.3). It was found that room temperature was sufficient to cause maximum oxidation in all samples used in this investigation. Since it is possible that some untested wastes might require higher temperatures for oxidation, it would be worthwhile in any routine analytical work to check the possibility of eliminating the heating step from the procedure.

The ODI test was also found to be insensitive to time. The relative percent transmittance was not effectively changed by either the period of time the samples were heated or the length of time after heating, before they were read in the spectrophotometer, as long as the insoluble salts had settled out.

Phase two of the experimental work attempted to compare the ODI test to established tests and formulate conversion factors which would help visualize the new test in the context of the old. It was found the ODI did not duplicate any of the older tests, not even the COD which uses the same dichromate oxidizer (FIGURE III.6). ODI values were compared to BOD, COD and TOC values resulting in a wide range of ratios. In effect every waste had a different conversion factor for every comparable ratio. The need for the individual analysis of each waste was emphasized. In a subsequent analysis of the ratios (TABLE B-IV) it was found that the ratio of ODI to COD had the least variation while those of the ODI to BOD and BOD to COD were approximately equal. This means that by using the ODI to BOD ratio to convert to BOD, an operator has at least as good a chance of approximating the true BOD as he does by using the COD to BOD ratio.

The ODI test was found to give reasonable measurements of treatment plant efficiency (TABLE B-VI). The fact that the values are higher than those calculated from BOD values, should not, in itself, be a cause for rejection, since different parameters are being measured. If absolute parity is desired, a series of tests could establish a conversion factor. A more reasonable approach would be

to accept the ODI efficiencies as calculated. Since efficiencies are relative terms, the adjustment to thinking in the new values would come quickly. The ODI efficiencies are faster and more precise than those calculated using BOD values. As such they allow treatment plant staff to make almost immediate process corrections as required. If, for comparison and record purposes, BOD's and BOD efficiencies are desired, these can be still run as before, but the day to day operation can be based on a comprehensive testing program using the ODI.

In CHAPTER I, the criteria of the ideal test were listed along with the statement that no existing test met them all. As a result of the foregoing experimental work, the ODI test can now be analyzed in terms of the ideal test criteria.

The first criterion was that a test have the ability to detect polluting (oxygen demanding) components in a waste. It has been shown that the ODI has the ability to detect organic material in a waste, given the limitations of the dichromate oxidizer as discussed in CHAPTER III.1. While not duplicating biological oxidation exactly, the dichromate chemical oxidation gives a reasonable approximation with most organic compounds. The fact that it is not susceptible to toxic material may be considered a limitation in pollution control work but would be an advantage in testing many industrial effluents.

The second criterion states that a test should have the ability to measure polluting components quickly and with reasonable precision. The ODI is a very fast test, which can be run within 30

minutes. If experiments on a particular waste show that the boiling water bath step can be eliminated, the time of testing could be reduced to approximately 10 minutes. The precision of the ODI is good. Tests showed it to have a much lower coefficient of variation than the BOD test.

Criterion number three was that the test should enable prediction of how a stream or lake will react when the waste is introduced. Here the ODI is obviously inferior to the BOD, since chemical oxidation gives no idea of reaction rates, deoxygenation, or toxicity to organisms. Only a test involving biological reactions can predict these. However, the ODI may be useful in predicting ultimate oxygen depletion and oxygen demand loadings from waste sources.

The fourth criterion states that the test should be simple and economical. The reason for this is to enable its use by operators of small treatment plants and sewage lagoons in addition to large well equipped laboratories. The ODI has been shown to be well suited for use under these conditions. It requires no particular technical skill in the operator nor does it require complicated expensive equipment. The most expensive item required would be the spectrophotometer with a price in the area of five hundred dollars. The test has been shown to be insensitive to variations in test procedure. The only critical step was the amount of dichromate added. Precision can be assured by careful instruction of the operator as to proper pipetting technique.

It is hoped that the Oxygen Demand Index test will be seriously

considered for use by workers involved in waste treatment and pollution control. The ODI, like all other tests, has its limitations, but in areas where speed and precision are required and funds are limited, the Oxygen Demand Index provides a definite improvement over existing tests.

LIST OF REFERENCES

1. Blackmore, R.H., and Voshel, D., "Rapid Determination of Total Organic Carbon (TOC) in Sewage", Water and Sewage Works 114 (398) 1967.
2. BUSCH, A.W., "Carbon Analysis as a Concept and Procedure in Water Pollution Technology", Analyzer, 8, 1,3, (1967).
3. Clifford, D.E., "Automatic Measurement of Total Oxygen Demand", 23rd Annual Purdue Industrial Waste Conference, May, 1968 (to be published).
4. Dzyadzio, A.M., Vodosnabzhenenie i Sanit. Tekh., No. 8-9, (1938) (unavailable).
5. Fair, G.M., and Geyer, J.C., Water Supply and Waste-Water Disposal, Jon Wiley & Sons, Inc., New York (1967).
6. Ford, D.L., "Total Organic Carbon as a Waste Water Parameter", Public Works, 99(4), 1968.
7. Foulds, J.M., and Lundsford, J.V., "An Analysis of the COD Method", Water and Sewage Works 115:112 (1968).
8. Hill, H.N., "Carbon Analysis", Union Carbide Corp. Publication (1969).
9. Jeris, John A., "A Rapid COD Test", Water and Wastes Engineering, 4:89 (1967).
10. Keiselbach, R., "Continuous Recording of Concentration of Organic Matter in Waste Water", Anal. Chem., 26:8(1954).
11. Klein, L.J., Proceedings of the Institute of Sewage Purification (England), (1941). (Unavailable).
12. Larson, T.E., Sollo, F.W., and Gruner, B.J., "The Determination of Total Organic Carbon in Water", Purdue University Eng. Bull. Extension Service, 117, (1964).
13. Moore, W.A., Kroner, R.C., and Ruchhoft, C.C., "Dichromate Reflux Method for Determination of Oxygen Consumed", Anal. Chem., 21:953 (1949).

14. Mukherjee, S.K., Chatterji, A.K., and Saraswat, I.P., "Effect of pH on the Rate of BOD of Waste Water", Journal Water Pollution Control Federation 40(11) pt. 1 (1968).
15. Sawyer, C.N., and McCarty, P.L., Chemistry for Sanitary Engineers McGraw-Hill Book Company, Inc., New York, (1967).
16. Schaffer, R.B., et al, "Application of a Carbon Analyzer in Waste Treatment", Journal Water Pollution Control Federation 37,11 1545 (Nov. 1965).
17. Standard Methods for the Examination of Water and Wastewater, American Public Health Association, New York, (12th Ed. 1965).
18. Stenger, V.A., and Van Hall, C.E., "Rapid Method for Determination of COD" Anal. Chem., 39:2 (1967)
19. Van Hall, C.E., Safranko, J., and Stenger, V.A., "A Rapid Combustion Method for Determination of Organic Substances in Aqueous Solutions", Anal. Chem., 35:315 (1963).
20. Van Hall, C.E., Barth, Dennis and Stenger, V.A., "Elimination of Carbonates from Aqueous Solutions Prior to Organic Carbon Determinations", Anal. Chem. 37 (1965).
21. Wells, W.N., "Evaluation of the Jeris Rapid COD Test" Water and Sewage Works, 117:4 (April 1970).
22. Westerhold, A.F., "Oxygen Demand Index", presented at Annual Operators Conference, Springfield, Illinois, April 8, 1964.
23. Williams, R.T., "Analyzer Looks for Organic Carbon" Instrumentation Technology, 14, 2, 63 (1967).

APPENDIX A
PROCEDURE FOR THE
OXYGEN DEMAND INDEX

PROCEDURE FOR THE OXYGEN DEMAND INDEX
(Using COD Reagents)

PRINCIPLE:

This test is a modification of the dichromate oxygen demand test. The dichromate is reduced from the yellow hexavalent to the green trivalent state by organic material in a sample. The amount of green color produced is measured colorimetrically to give an approximate measure of sample strength in a short period of time.

SAMPLE:

At least 5 ml sample is required.

EQUIPMENT:

1. Barnstead water bath, model WB 100 or other means or providing a boiling water bath. (A kettle of water boiling or an electric hot plate or Bunsen burner is satisfactory).
2. Bausch and Lomb Spectronic 20 with 1 inch cell holder or equal.
3. Test tube rack to hold 1 inch test tubes (made locally).

REAGENTS:

1. Potassium dichromate, A.R. ($K_2Cr_2O_7$).
2. Mercuric sulfate, A.R. ($HgSO_4$).
3. Dextrose (glucose) crystal, reagent or pure bacterial grade, anhydrous.

4. Silver sulfate, A.R. (Ag_2SO_4).
5. Sulfuric acid, conc. A.R. (H_2SO_4).

SOLUTIONS:

1. Standard 0.25N dichromate solution. Dissolve 12.259 g $\text{K}_2\text{Cr}_2\text{O}_7$ reagent grade (dried at 103°C for 2 hours) in distilled water and dilute to 1000 ml.
2. Sulfuric acid, silver sulfate reagent. Add 22 g silver sulfate (Ag_2SO_4) per 9 lb bottle of conc. sulfuric acid. Invert bottle occasionally to aid in dissolution (1 to 2 days may be required).
3. Standard glucose solution used for making calibration curve. Dissolve 0.600 g glucose (dried at 103°C for 1 hour) in distilled water and make up to 1000 ml. (This solution should have a BOD of 448 ± 20 mg/l; see Standard Methods, (12th Edition), pages 418-419. One ml of this solution has an Oxygen Demand Index (ODI) value of 90 based on BOD tests).

PROCEDURE:

1. Place 25 mm x 150 mm test tubes in rack (1 for blank and 1 for each sample).
2. Add 0.1 g mercuric sulfate powder (approximately with a Hach Chemical Company #510 or equal measuring spoon) to each tube.
3. Add with pipet 5.0 ml distilled water into blank tube.

4. Add with pipet 5.0 ml sample (or aliquot made up to 5.0 ml) into each sample tube and swirl to mix.
5. Add exactly with pipet 1.5 ml of 0.25N dichromate solution.
6. Add carefully 7.5 ml of the sulfuric-acid silver sulfate reagent.
7. Mix well by swirling tube.
8. Place rack containing blank and sample tubes in boiling water bath for 20 minutes.
9. Remove, cool in water or let stand to cool. This also allows time for HgSO_4 and other suspended material to settle.
10. Read in Spectronic 20 at 600 mu, using reagent blank for 100 percent.
11. Calculate ODI value from graph prepared by running 0.0, 1.0, 2.0, 3.0, 4.0, and 5.0 ml volumes of 600 mg/l glucose solution. (1.0 ml has an ODI value of 90). See calibration curve, FIGURE III.1.

REPORTING:

Report as ODI.

SIGNIFICANCE:

On samples containing bio-degradable material the ODI values should be roughly equivalent to BOD values. Samples containing non-bio-degradable material oxidizable by dichromate may give high values.

APPENDIX B
DETAILED DATA AND PLOTS

TABLE B-I
OXYGEN DEMAND TEST DATA - EDMONTON

Sample Source	BOD mg/l	COD mg/l	ODI mg/l	RATIOS		
				$\frac{\text{BOD}}{\text{COD}}$	$\frac{\text{ODI}}{\text{BOD}}$	$\frac{\text{ODI}}{\text{COD}}$
Edmonton Raw Sewage	263	464	222	0.57	0.84	0.48
	244	367	160	0.67	0.66	0.44
	240	367	180	0.65	0.75	0.49
	206	442	200	0.47	0.97	0.45
	209	405	160	0.52	0.77	0.39
	255	403	155	0.63	0.61	0.38
	270	476	180	0.57	0.67	0.38
	295	493	190	0.60	0.64	0.39
Means				0.58	0.73	0.42
Standard Deviation				0.07	0.12	0.046
Edmonton #3 Plant Primary Effluent	68	167	65	0.41	0.95	0.39
	94	296	98	0.32	1.0	0.33
	77	106	25	0.73	0.36	0.24
	180	325	115	0.55	0.64	0.35
	195	350	135	0.56	0.69	0.39
	176	284	125	0.62	0.71	0.44
	65	95	38	0.68	0.59	0.40
	120	178	80	0.67	0.67	0.45
Means				0.56	0.70	0.37
Standard Deviation				0.14	0.20	0.07

TABLE B-II
OXYGEN DEMAND TESTS DATA - MISCELLANEOUS SOURCES

Sample Source	BOD mg/l	COD mg/l	ODI mg/l	RATIOS		
				$\frac{\text{BOD}}{\text{COD}}$	$\frac{\text{ODI}}{\text{BOD}}$	$\frac{\text{ODI}}{\text{COD}}$
Devon Raw Sewage	170	330	135	0.52	0.80	0.41
	137	297	115	0.46	0.84	0.39
	210	338	145	0.62	0.69	0.43
	240	690	265	0.35	1.10	0.38
Means				0.48	0.85	0.40
Standard Deviation				0.11	0.17	0.022
Devon Primary Effluent	102	220	77	0.46	0.76	0.35
	90	203	80	0.44	0.89	0.39
	154	206	78	0.75	0.51	0.38
	60	172	50	0.35	0.83	0.29
Means				0.50	0.74	0.35
Standard Deviation				0.17	0.16	0.047
Devon Trickling Filter Effluent	45	75	25	0.60	0.56	0.33
	104	154	70	0.70	0.67	0.46
	33	49	21	0.67	0.64	0.43
	48	125	28	0.38	0.58	0.22
Means				0.58	0.61	0.36
Standard Deviation				0.14	0.051	0.10
Leduc Lagoons	120	312	120	0.39	1.00	0.39
	18	59	18	0.31	1.00	0.31
Calgary Primary Effluent	178	326	158	0.55	0.89	0.46
	120	220	125	0.55	1.04	0.57

TABLE B-III

OXYGEN DEMAND TESTS DATA - CALGARY AREA WASTES

Sample Source	RATIOS						
	BOD mg/l	COD mg/l	ODI mg/l	TOC mg/l	$\frac{\text{BOD}}{\text{COD}}$	$\frac{\text{ODI}}{\text{BOD}}$	$\frac{\text{ODI}}{\text{COD}}$
Calgary Raw Sewage	146	358	190	99	0.41	1.30	0.53
	144	348	168	102	0.41	1.17	0.48
	123	348	180	120	0.35	1.46	0.52
	135	289	125	102	0.47	0.93	0.43
	111	315	154	108	0.35	1.39	0.49
	105	280	118	108	0.38	1.12	0.42
	57	174	76	69	0.33	1.33	0.44
Means					0.38	1.24	0.47
Standard Deviation					0.048	0.18	0.044
Box Factory	2270	5920	1554	1630	0.38	0.68	0.26
Brewery 1	570	730	425	296	0.78	0.75	0.58
Brewery 2	804	2600	1484	2550	0.31	1.85	0.57
Chemical Plant	2600	7740	5800	2760	0.34	2.23	0.75
Packing Plant	7050	10650	5000	4020	0.66	0.71	0.47

TABLE B-IV
COEFFICIENTS OF VARIATION* FOR OXYGEN
DEMAND TEST RATIOS

Sample Source	Coefficient of Variation for Ratio:			
	$\frac{ODI}{BOD}$	$\frac{ODI}{COD}$	$\frac{ODI}{TOC}$	$\frac{BOD}{COD}$
Edmonton Raw Sewage	16.3%	10.9%	---	11.5%
Edmonton Primary Effluent	28.7%	18.1%	---	24.7%
Calgary Raw Sewage	14.7%	9.3%	20.8%	12.4%
Devon Raw Sewage	20.3%	5.5%	---	23.2%
Devon Primary Effluent	22.4%	13.2%	---	34.6%
Devon Final Effluent	8.34%	29.2%	---	24.5%
Means	18.4%	14.4%	20.8%	21.8%

*Standard Deviation divided by the mean

TABLE B-V
RELATIVE EFFECT OF SUSPENDED AND DISSOLVED
ORGANIC SOLIDS ON OXYGEN DEMAND TESTS

Sample No.	Conc.	SUSPENDED			Conc.	DISSOLVED		
		BOD	COD	ODI		BOD	COD	ODI
1	84*	47	137	55	138	63	147	55
2	114	47	137	55	118	63	147	55
3	62	34	117	65	190	96	221	80
4	90	34	117	64	198	96	221	80
5	322	110	445	176	218	130	245	89
6	324	110	445	176	228	130	245	89
7	136	50	282	115	170	110	194	65
8	168	50	282	115	154	110	194	65
9	178	110	330	135	124	90	163	55
10	206	110	330	135	144	90	163	55

*All values in mg/l

TABLE B-VI
TREATMENT PLANT EFFICIENCIES - DEVON
GRAB SAMPLES JULY 1970

		BOD mg/l	COD mg/l	ODI mg/l
Run 1	Raw	170	330	135
	Primary	102	220	77
	Final	45	75	25
Primary Efficiency		40%	33%	43%
Plant Efficiency		73.5%	77.4%	81.5%
Run 2	Raw	137	297	115
	Primary	90	203	80
	Final*	104	154	70
Primary Efficiency		34.3%	31.6%	30.5%
Plant Efficiency		*Pumps off		
Run 3	Raw	210	338	145
	Primary	154	206	78
	Final	33	49	21
Primary Efficiency		26.7%	39%	46.1
Plant Efficiency		84.4%	85.5	85.5
Run 4	Raw	240	690	265
	Primary	60	172	50
	Final	48	125	28
Primary Efficiency		75%	75%	81%
Plant Efficiency		80%	82%	89.5%
AVERAGES:				
Primary Efficiency		44%	44.6%	50.1%
Plant Efficiency		79.2%	81.6%	85.5%

TABLE B-VII

OXYGEN DEMAND TEST DATA - MISCELLANEOUS SOURCES
 (Courtesy - Environmental Health Services Laboratory, Edmonton)

Sample Source	ODI mg/l	BOD mg/l	RATIO $\frac{\text{ODI}}{\text{BOD}}$
Edmonton Raw Sewage	270 305 430	300 355 301	0.90 0.86 1.43
Edmonton Final Effluent	40 100 60	49 32 47	0.82 3.1 1.28
Edmonton #3 Plant Raw Sewage	200 135 270	233 150 175	0.86 0.90 1.54
Edmonton #3 Plant Primary Effluent	220 60 150	241 123 110	0.91 0.49 1.36
Red Deer Primary Effluent	220 175	166 213	1.32 0.81
Raw Sewage	255	2.55	1.00
Pulp Mill Waste	415 350	100 120	4.15 2.92
Refinery Waste	30 60 40 100 70	13 26 28 54 68	2.30 2.30 1.43 1.86 1.03

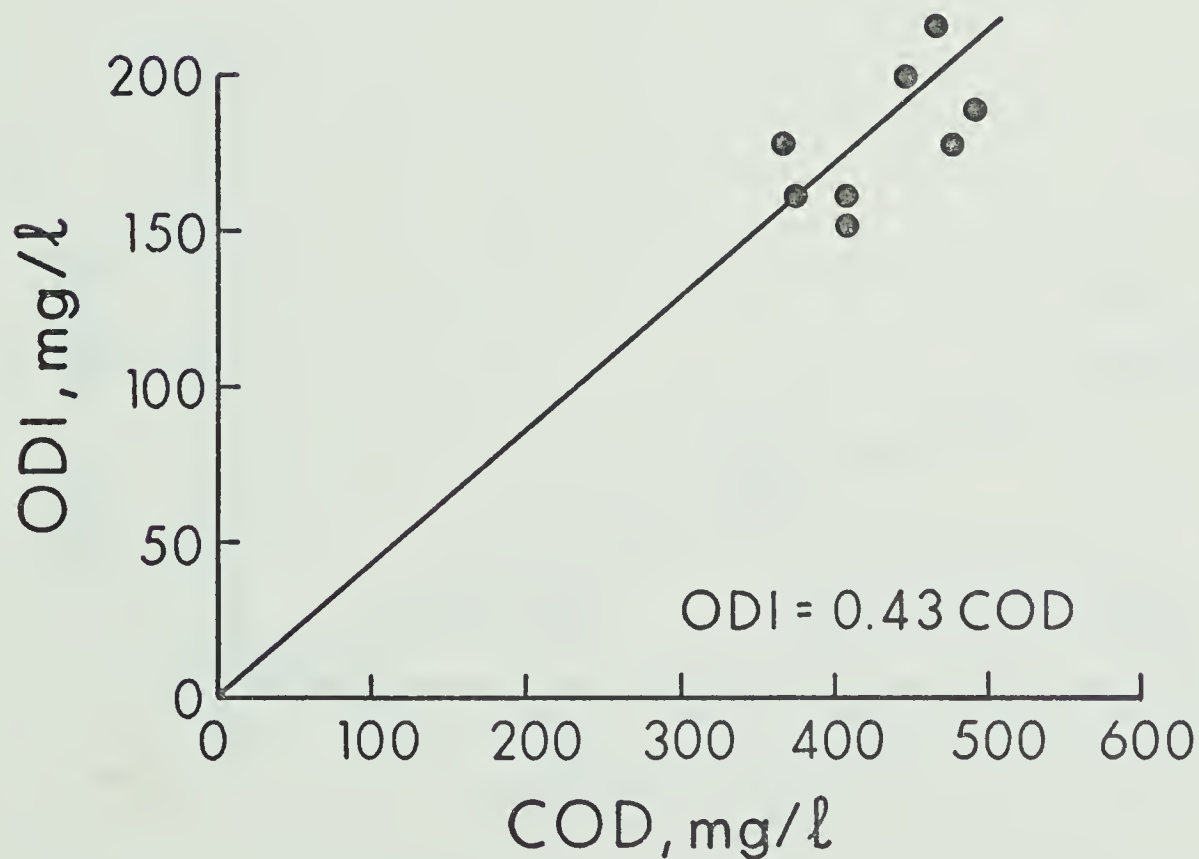
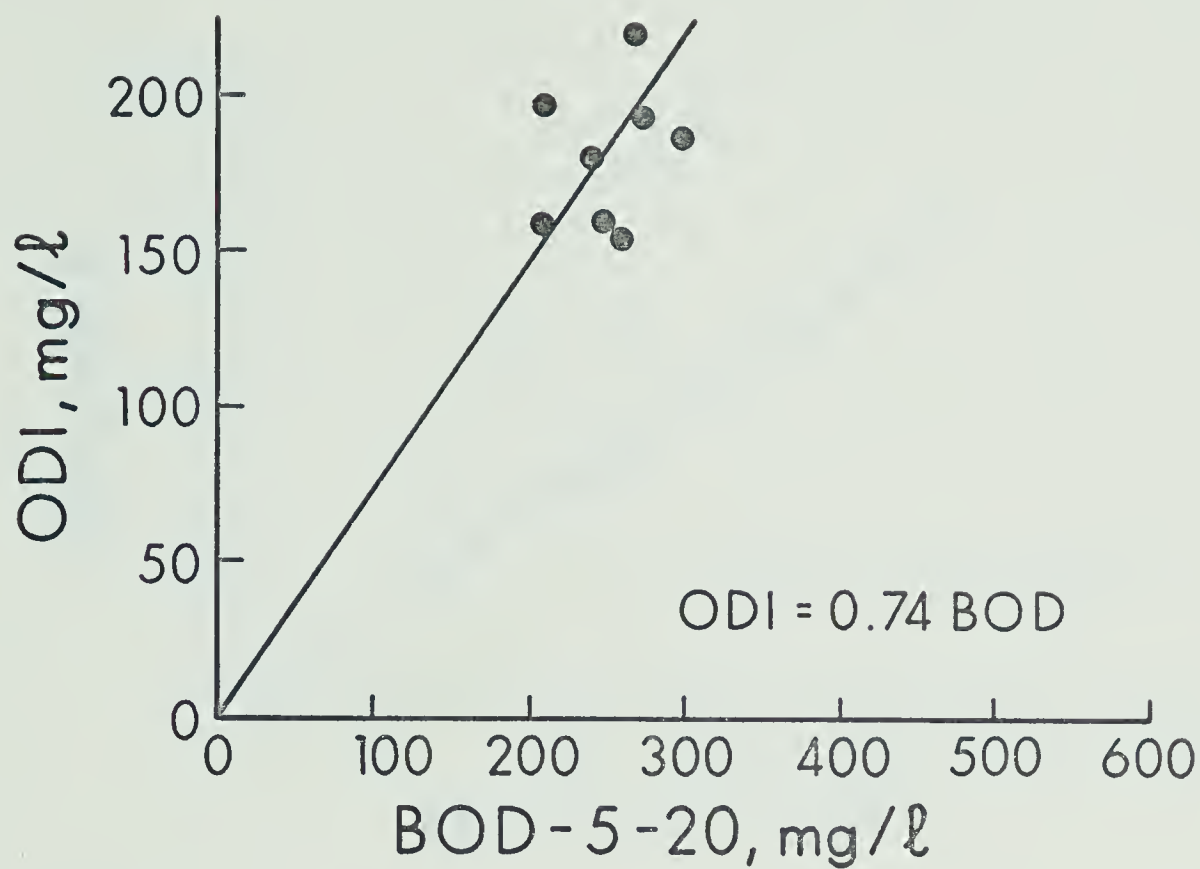


FIG: B.1 COMPARISON OF ODI VALUES WITH BOD AND COD - EDMONTON RAW SEWAGE

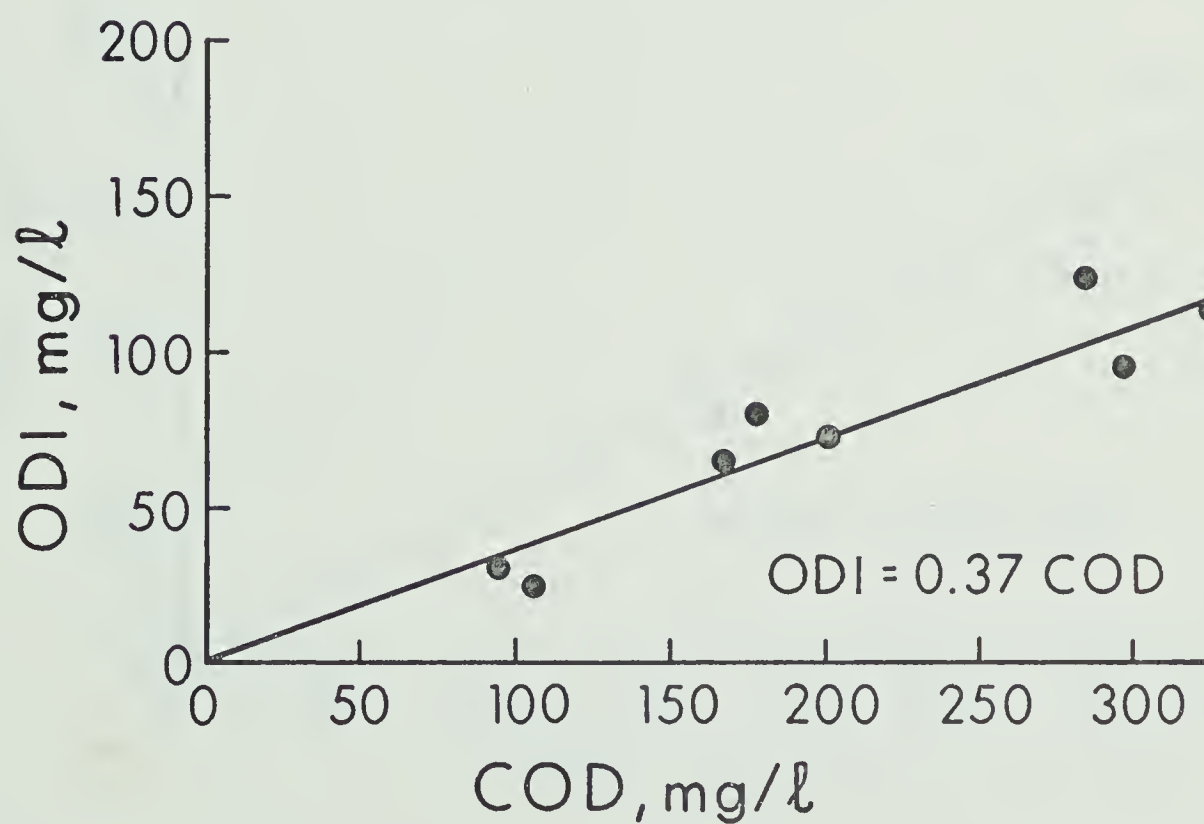
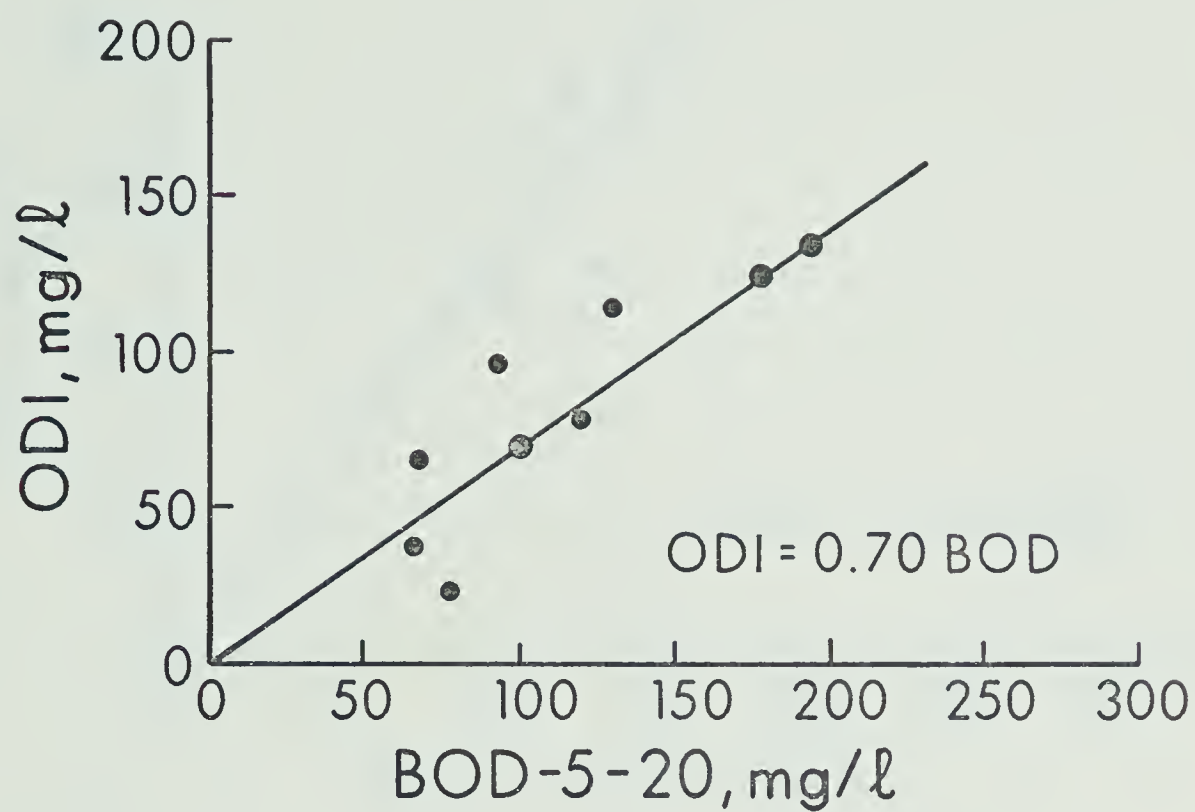


FIG: B.2 COMPARISON OF ODI VALUES WITH BOD AND COD - EDMONTON PRIMARY EFFLUENT

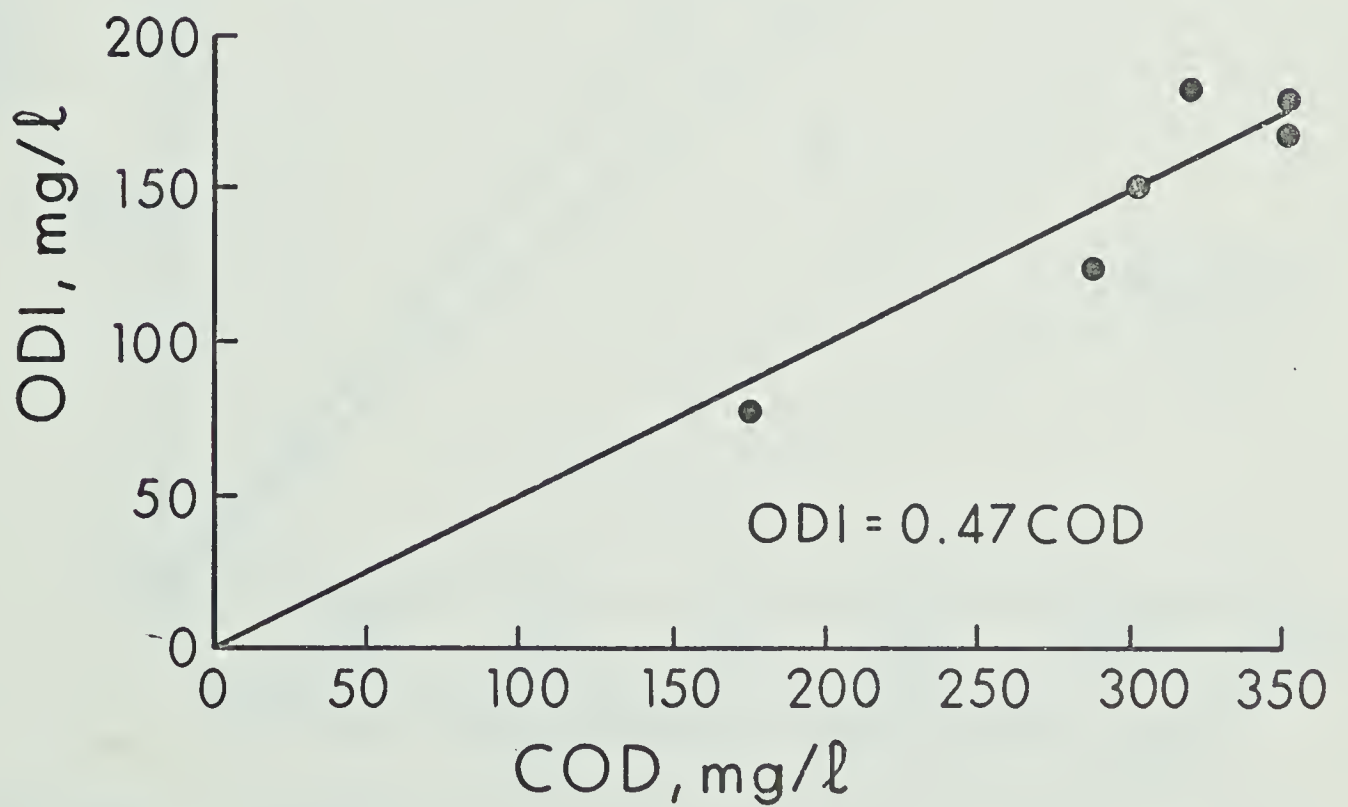
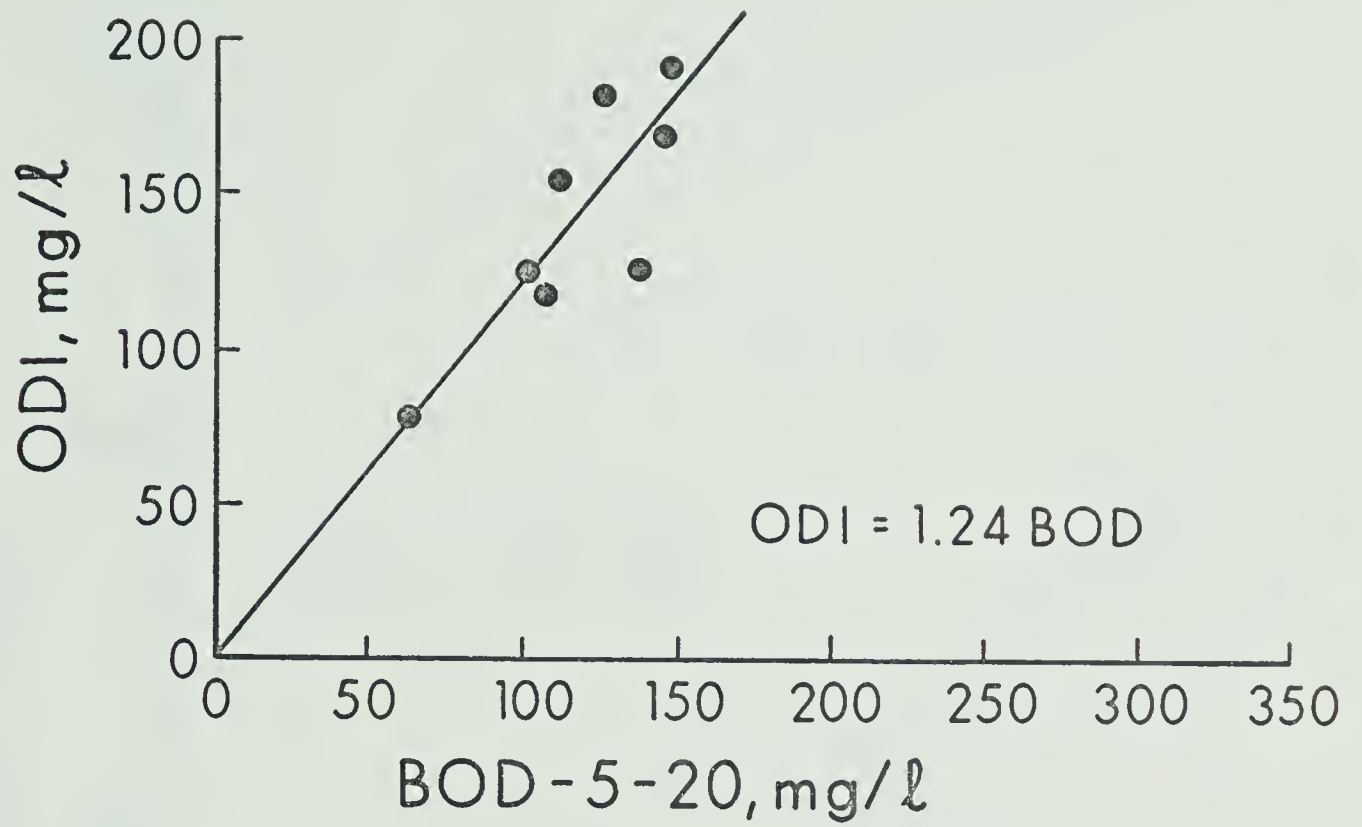


FIG: B.3 COMPARISON OF ODI VALUES WITH BOD AND COD - CALGARY RAW SEWAGE

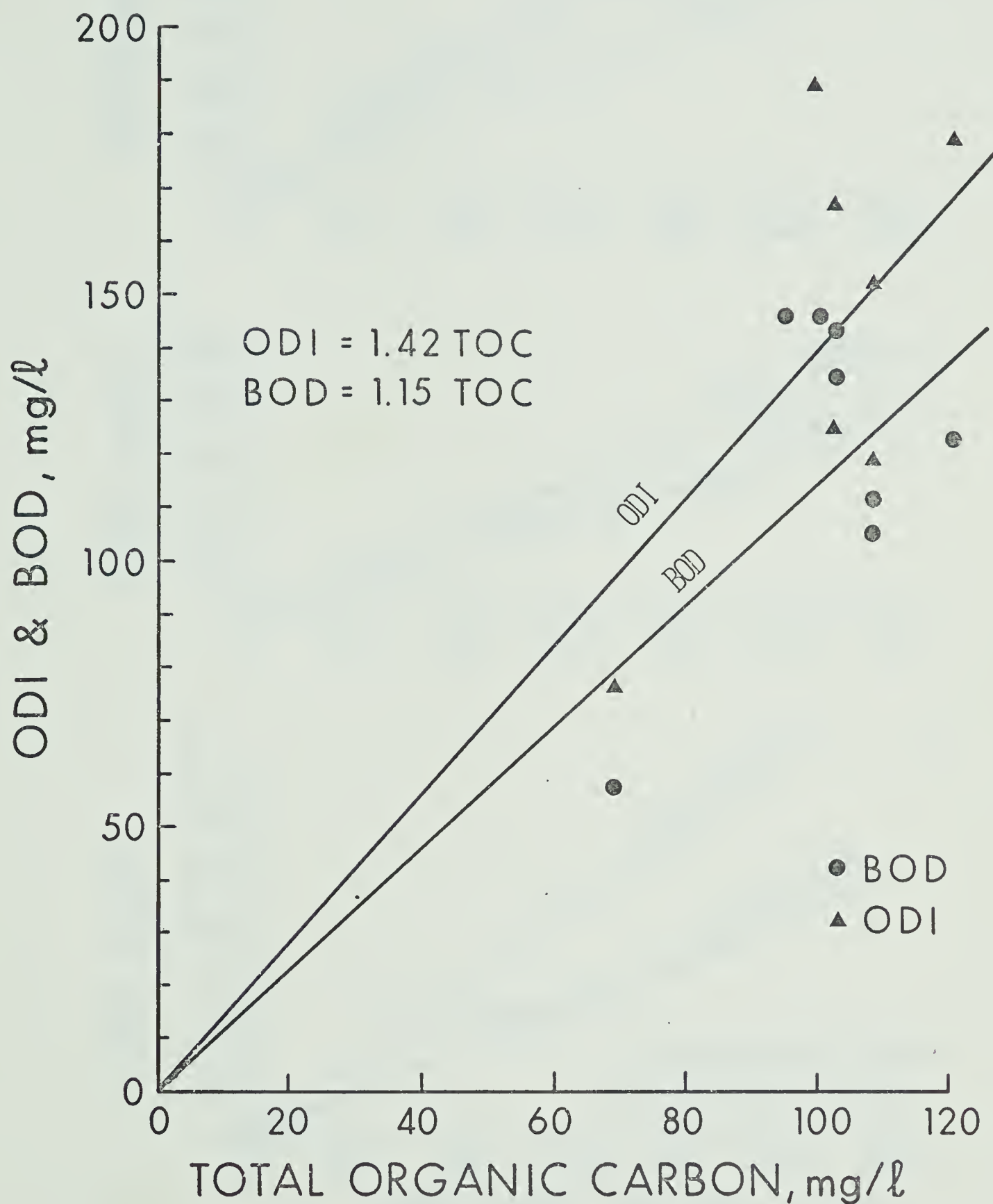


FIG. B.4 COMPARISON OF TOC VALUES WITH BOD AND ODI
- CALGARY RAW SEWAGE

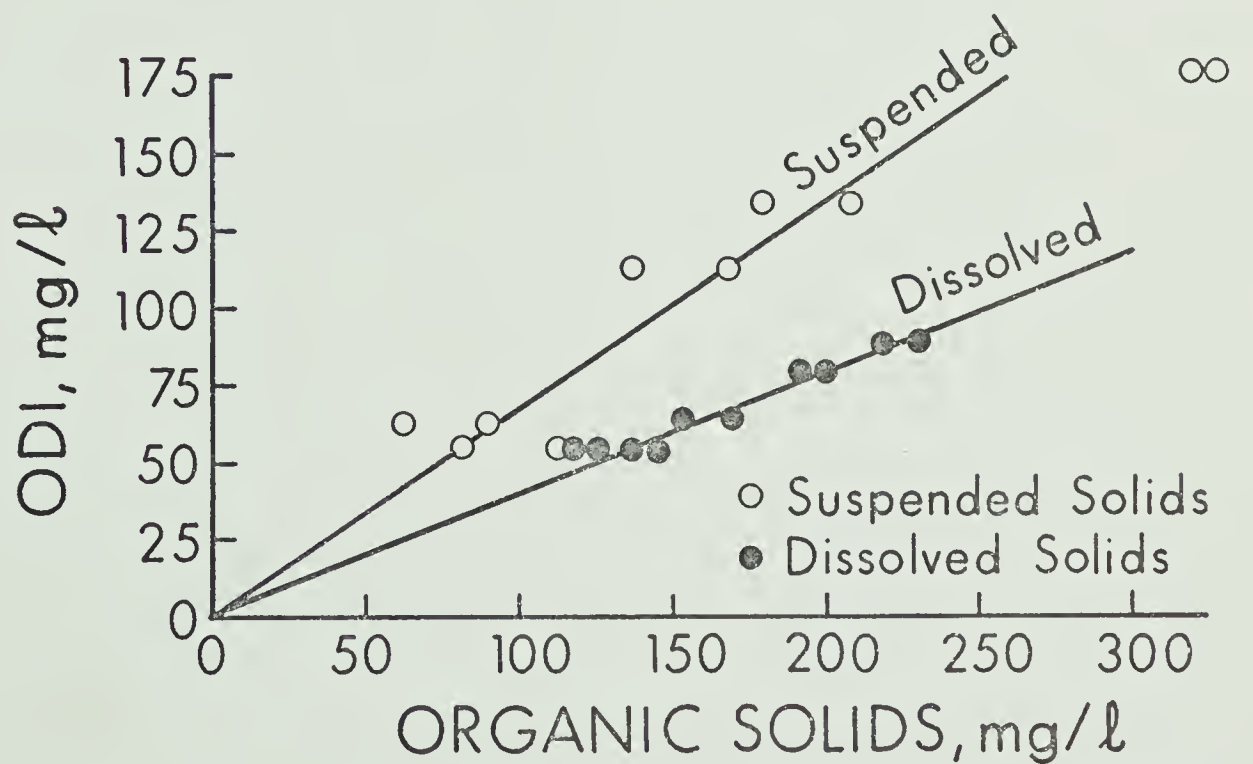
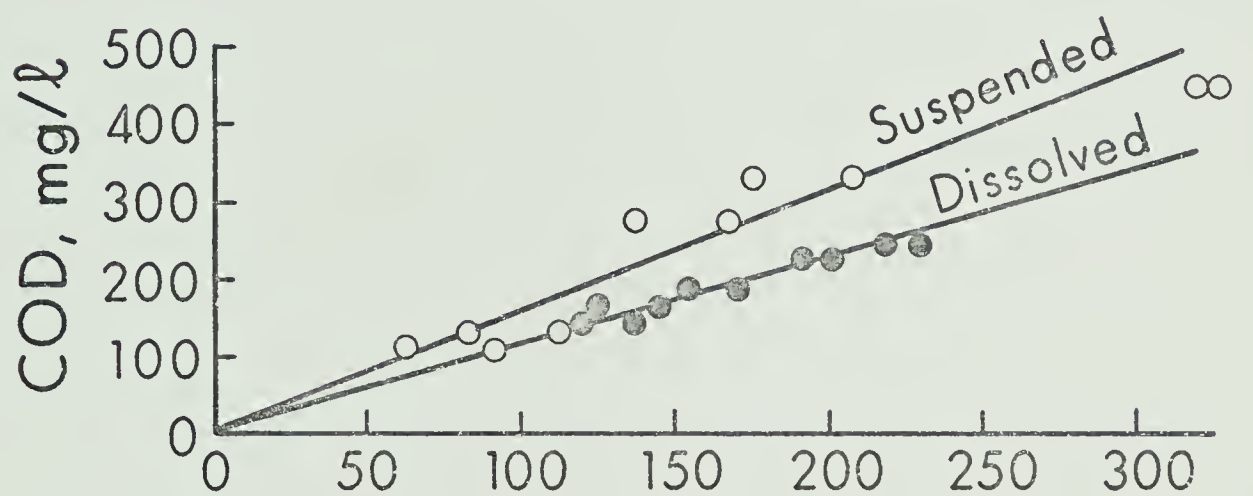
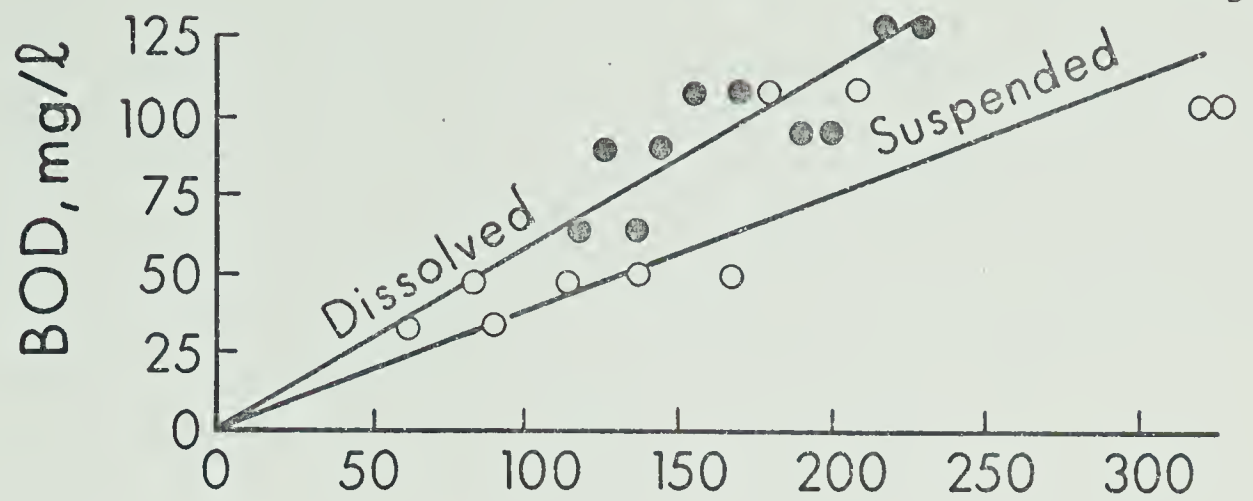


FIG: B.5 RELATIVE EFFECT OF SUSPENDED AND DISSOLVED SOLIDS ON OXYGEN DEMAND TESTS (Edmonton and Devon Raw Sewage)

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